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Experimental & Theoretical Studies of Solid Solution Formation in Lime & Limestone SO2 Scrubbers. Vol I. Final Report

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EXPERIMENTAL AND THEORETICAL STUDIES OF SOLID SOLUTION FORMATION IN LIME AND LIMESTONE SO_2 SCRUBBERS

VOLUME I. FINAL REPORT

by

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ABSTRACT

This report describes the results of the theoretical and experimental program that Radian conducted to characterize the coprecipitation of calcium sulfate with calcium sulfite hemihydrate.

The existence of a coprecipitation product had been hypothesized to explain the mechanism by which sulfate could be precipitated from a scrubber solution subsaturated with respect to calcium sulfate. Long term, steady-state operation of lime and limestone SO_2 scrubbing systems with oxidation rates below 20% has been achieved with liquors subsaturated with respect to all known calcium sulfate solid forms. Nevertheless, sulfate is measured in the solids precipitated from these systems.

The existence of a calcium sulfate-calcium sulfite solid solution has been confirmed experimentally and a theoretical formulation has been established. Calcium sulfite hemihydrate was precipitated under controlled laboratory conditions from solutions subsaturated in calcium sulfate. Specific chemical analysis and infrared spectroscopic techniques were used to identify sulfate in the solids.

The sulfate content in the precipitate was studied as a function of the relative saturation of calcium sulfate and the precipitation rate of calcium sulfite hemihydrate. Also, the effects of high magnesium and chlorides concentrations and limestone and lime dissolution on the sulfate content of the solids were measured.

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DISCLAIMER

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1.0 SUMMARY AND CONCLUSIONS

An experimental and theoretical study of the calcium sulfite-sulfate solid solution formation has been conducted for the Environmental Protection Agency (EPA) by Radian Corporation. Radian has confirmed the hypothesis of R. H. Borgwardt and others that the sulfate is removed from solution during subsaturated ($CaSO_4 \cdot 2H_2O$) operation in pilot plant tests by the formation of a "solid solution" of calcium sulfite and calcium sulfate. The sulfite oxidation rate has been identified by Radian as the critical control parameter for operation of the SO_2 scrubber subsaturated with respect to gypsum.

This report does not contain a complete explanation of all of the experimental and field data that have been accumulated relating to the coprecipitation of sulfate with calcium sulfite hemihydrate. Nor is a theoretical expression offered that accounts for all of the experimental results obtained from this program. The problem may be a result of several factors including:

- difficulties associated with control of all experimental variables and
- incomplete understanding of all the factors involved in the phenomenon of coprecipitation.

The experimental data of this program are presented in this report along with a critical assessment of the validity of the data. On the positive side, this study has shown that the strongest correlating factor relating to the sulfate content of the coprecipitate is the relative saturation of calcium

sulfate hemihydrate in the aqueous phase. This and the demonstrated absence of a major kinetic effect indicate that the coprecipitation of sulfate with calcium sulfite hemihydrate is basically an equilibrium controlled process.

This work has successfully shown the existence of a solid solution of sulfate with calcium sulfite hemihydrate by direct verification using infrared spectroscopy. A relationship has also been formulated to predict the sulfate content of the solids during subsaturated (gypsum) operation based on the solution composition.

A summary of the results of this program follows.

1.1 Verification of the Existence of the Calcium Sulfite-Sulfate Solid Solution

Chemical analyses of solids precipitated from solutions prepared under controlled laboratory conditions to be supersaturated in $CaSO_3 \cdot \frac{1}{2}H_2O$ and subsaturated in $CaSO_4 \cdot 2H_2O$ have verified the presence of sulfate. Infrared spectral analysis was also used to confirm the presence of sulfate in the solids.

X-ray diffraction patterns of the sulfate-containing solids were essentially indistinguishable from the patterns of pure $CaSO_3 \cdot \frac{1}{2}H_2O$. No separate crystalline phase containing sulfate could be identified by this method.

The infrared spectra not only were used to substantiate the presence of sulfate in the solids, but also provided direct evidence of the existence of a coprecipitation product. The absorption patterns in the 1100-1200 cm^{-1} region assigned to the sulfate ion are quite different for sulfate as a pure gypsum phase from sulfate in solid solution.

To determine whether the coprecipitate is in thermodynamic equilibrium with the solution from which it is grown or is a result of kinetic effects, some long-term equilibration tests were conducted. Solids were allowed to come to equilibrium with solutions containing calcium, sulfate and magnesium concentrations identical to their concentrations in the solutions from which the solids were precipitated. After as long as four weeks, the liquid phase was found to be saturated with calcium sulfite hemihydrate and still subsaturated in calcium sulfate dihydrate. The sulfate content of the solids did not change substantially during these tests.

1.2 Quantitative Measurement of the Sulfate Content of the Calcium Sulfite-Sulfate Solid Solution

An analytical technique was developed during this program for the specific determination of sulfate in solids typically precipitated in lime and limestone-based SO_2 scrubbers. Previously, the sulfate concentration measurements were obtained by a difference technique. A portion of the sample was analyzed for total sulfite. A second portion treated to oxidize all of the sulfite to sulfate was then analyzed for sulfate. The difference in these two values gives the original sulfate value. When the sulfate level is low compared to the sulfite concentration, the error of this technique becomes quite large.

The specific sulfate technique selected for this program can be used to determine sulfate concentrations in the range of interest to within ±5% of the actual value, e.g. $10 \pm .5\%$.

Infrared analysis was also used to quantitatively measure the sulfate concentrations in the solid solution samples. The infrared spectral technique was calibrated by initially ratioing the solid solution sulfate absorptivity at 1220 cm^{-1}

to the absorptivity of the water of hydration band at 1620 cm^{-1}. A correlation was then established relating this ratio to the sulfate content as determined chemically. Though not as sensitive as the specific sulfate technique, the infrared technique is much faster and can also be used to distinguish the forms of sulfate present.

1.3 Development of Sampling Methods for Slurries Containing High-Liquid Phase Magnesium Concentrations

One of the difficult problems in characterizing the solids precipitated from solutions containing high magnesium concentrations is the contamination of the solids by the high concentration of dissolved magnesium sulfate. This contamination results from the adhesion of the liquid phase to the filtered solids with subsequent crystallization of the magnesium sulfate during drying. Sampling and sample handling techniques have been developed which minimize this interference.

1.4 Effect of Relative Saturation of Calcium Sulfate Hemihydrate

The calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) relative saturation has been determined to be the most significant correlating variable associated with the formation of the calcium sulfite-sulfate solid solution in the laboratory studies conducted by Radian. These studies have shown that the sulfate content of the solids, i.e., the sulfate mole fraction of the precipitated solids, varies most rapidly from 0 to 0.12 as the calcium sulfate hemihydrate relative saturation ranges from 0 to 0.20. The sulfate mole fraction in the solid solution rises to 0.16 at a hemihydrate relative saturation of 0.45, the point at which the solution is also saturated with respect to gypsum.

These results are consistent with the theory developed in early phases of the experimental program which states that the equilibrium contribution to the sulfate content of the solid solution will be a function of the calcium sulfate hemihydrate relative saturation. The relationship that predicts the sulfate mole fraction from the relative saturation is given in Equation 1-1.

$$RS_{CaSO_4 \cdot \frac{1}{2}H_2O} = x_{CaSO_4 \cdot \frac{1}{2}H_2O} \cdot \exp(15.9 x_{CaSO_4 \cdot \frac{1}{2}H_2O} - 1.45) \qquad (1\text{-}1)$$

where,

$RS_{CaSO_4 \cdot \frac{1}{2}H_2O}$ = the relative saturation of calcium sulfate hemihydrate in the liquid phase, and

$x_{CaSO_4 \cdot \frac{1}{2}H_2O}$ = the mole fraction of sulfate in the solid phase.

1.5 Effect of the Calcium Sulfite Precipitation Rate

Experimental results have shown the calcium sulfite precipitation rate does not have a measurable effect on the amount of sulfate coprecipitated with calcium sulfite as a solid solution. This was true for precipitation from solutions both high and low in magnesium concentrations. In other words, kinetic effects do not appear to be significant in the composition of solid solution within the precipitation range studied, namely 0.001-1.7 millimoles/g-min. These results in conjunction with the calcium sulfate relative saturation data imply that for all practical purposes the composition of the calcium sulfite-sulfate solid solution is determined by an equilibrium condition and not simply by inclusion.

1.6 Effect of Magnesium and Carbonate Liquid-Phase Concentration on the Precipitation Rate of Calcium Sulfite Hemihydrate

Preliminary data from several kinetic experiments show that liquid-phase magnesium and carbonate ions may inhibit the precipitation rate of calcium sulfite hemihydrate. Nucleation in a calcium chloride-sodium sulfite system normally occurs at a calcium sulfite hemihydrate relative saturation of approximately 3.0. With the addition of magnesium, calcium sulfite hemihydrate relative saturations of 8-15 have been observed at precipitation rates significantly lower than those observed in the pure system indicating a decrease in the nucleation rate. The addition of the carbonate ion to a calcium sulfite-sulfate system required a $CaSO_3 \cdot \frac{1}{2}H_2O$ relative saturation of 5.3 to obtain the same precipitation rate measured at a relative saturation of 2.3 in a carbonate-free solution.

The implication of these observations may have a significant impact on SO_2 scrubber system design and warrant additional experimental studies.

1.7 Coprecipitation of Calcium Carbonate with the Calcium Sulfite-Sulfate Solid Solution

Qualitative results from infrared spectral analyses of solids precipitated from liquors containing carbonate indicate that carbonate is coprecipitated with the calcium sulfite-sulfate solid solution. This is particularly evident in the I.R. spectra of scrubber solids from Pennsylvania Power & Light's Sunbury pilot unit where evidence of matrix isolated carbonate was observed. This coprecipitation of carbonate impacts on the maximum limestone utilization which can be achieved and may have an effect on the sulfite to sulfate ratio that can be coprecipitated. Based on these results, additional study of the coprecipitation of carbonate with the calcium sulfite-sulfate solid solution is recommended.

2.0 BACKGROUND AND APPROACH

Pilot plant studies conducted by EPA at Research Triangle Park and full-scale operation at various plants in the U.S., Japan and England have demonstrated that both lime and limestone SO_2 scrubbers can operate unsaturated with respect to gypsum even under tight "closed-loop" operation. This fact offers an opportunity, if the phenomenon responsible can be understood and controlled, to effectively reduce gypsum-scaling potential which has persisted as one of the principal reliability problems of lime and limestone flue gas desulfurization systems.

The formation of a "solid solution" of calcium sulfite and calcium sulfate has been suggested by R. H. Borgwardt and others as the probable mechanism responsible for the sulfate purge which leads to unsaturated operation. Several variables such as sulfate concentration, sulfite precipitation rate and concentration of chloride and magnesium have been identified from field studies as influencing the composition of the solid solution.

Radian has conducted a theoretical and experimental study to characterize the chemical factors which affect the formation of the solid solution. The objectives of this study were to:

- develop a consistent theoretical basis for examining field and laboratory data,
- review available field data relative to unsaturated operation.

- develop, if necessary, sampling, sample handling, and analytical methods which are consistent with accurate measurement of sulfite and sulfate in both liquid and solid phases,

- study the application of physical and analytical techniques which can be used to establish direct evidence of the coprecipitation of sulfate with calcium sulfite hemihydrate,

- conduct equilibrium studies to establish whether or not a solid solution will precipitate from various solutions near equilibrium,

- conduct kinetic studies using a lime or limestone slurry and a clear liquor characteristic of either lime or limestone scrubbers to determine the effects of the sulfite precipitation rate, temperature and scrubber liquor composition with emphasis on magnesium and chloride, and

- develop a theoretical framework for liquid/solid equilibrium or kinetics in such a manner that it can be used for predicting conditions necessary for unsaturated operation of lime and limestone scrubbers as a function of liquor composition and oxidation.

3.0 THEORETICAL FRAMEWORK OF THE CALCIUM SULFITE-SULFATE SOLID SOLUTION

Coprecipitation may be controlled by equilibrium effects, kinetic effects, or a combination of the two. If a true solid solution is formed as a result of the coprecipitation of calcium sulfite and calcium sulfate, then fundamental thermodynamics can be used to describe the equilibrium relationships which control solid and liquid phase compositions. On the other hand, if sulfate tends to be incorporated into the solid phase by inclusion, then the kinetics of sulfite precipitation should be an important factor. In this latter case, the sulfate/sulfite ratio in the coprecipitated solids would be expected to be a direct function of the growth rate of calcium sulfite solids.

It is important to distinguish between these two possibilities for the following reasons. If the formation of a solid solution is the dominant mechanism of coprecipitation, the system sulfite oxidation rate will determine whether subsaturated operation is possible. On the other hand, if kinetic effects are significant, then system design (in addition to oxidation control) can be used to optimize coprecipitation and avoid sulfate scaling.

The existence of a solid solution in equilibrium with a liquid phase can be described thermodynamically through chemical potentials. The chemical potential, μ_{ij}, of the i^{th} component in the j^{th} phase may be written as:

$$\mu_{ij} = \mu^{\circ}_{ij} + RT\ell na_{ij} \qquad (3\text{-}1)$$

where: μ°_{ij} = the standard state chemical potential,

R = ideal gas constant,

T = the absolute temperature, and

a_{ij} = the activity of the $i^{\underline{th}}$ component in the $j^{\underline{th}}$ phase.

In this analysis, the following designations will apply.

$i = 1 \Rightarrow CaSO_3 \cdot \frac{1}{2}H_2O$

$i = 2 \Rightarrow CaSO_4 \cdot \frac{1}{2}H_2O$

$j = s \Rightarrow$ Solid

$j = \ell \Rightarrow$ Liquid

The standard state of the solid phase will be defined as the pure component. For a solid solution mixture, deviations from ideal solutions will be based on mole fractions. Solid phase activity coefficients, σ_i, are defined by Equation 3-2.

$$a_{1s} = \sigma_1 x_1 \qquad (3\text{-}2a)$$

$$a_{2s} = \sigma_2 x_2 \qquad (3\text{-}2b)$$

where the x's are the solid phase mole fractions.

The choice of the hemihydrate of calcium sulfate as the form of the solid phase was selected since the calcium sulfite host matrix is a hemihydrate. This situation can be imagined by simply replacing a sulfite ion with a sulfate ion. However, the mathematical formulation could be developed for the dihydrate of calcium sulfate equally as well. Direct measurement of the solids subsequently gave a mole ratio of total S to water of 2:1 which is consistent with the hemihydrate model.

The activities of $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot \frac{1}{2}H_2O$ in the liquid phase are defined in Equation 3-3:

$$a_{1\ell} = a_{Ca^{++}} a_{SO_3^{=}} a_{H_2O}^{\frac{1}{2}} \qquad (3\text{-}3a)$$

$$a_{2\ell} = a_{Ca^{++}} a_{SO_4^{=}} a_{H_2O}^{\frac{1}{2}} \qquad (3\text{-}3b)$$

The liquid phase is in equilibrium with the solid phase when the chemical potentials of all components in both phases are equal. Equating chemical potentials gives Equation 3-4.

$$\mu_{is} = \mu_{i\ell} \qquad (3\text{-}4)$$

Substituting the definitions in Equations 3-1 and 3-2 into 3-4 gives Equation 3-5.

$$\mu_{is}^{\circ} + RT \ln \sigma_i x_i = \mu_{i\ell}^{\circ} + RT \ln a_{i\ell} \qquad (3\text{-}5)$$

Equation 3-5 may be solved for the activities:

$$\frac{a_{i\ell}}{\sigma_i x_i} = e^{-(\mu^\circ_{i\ell} - \mu^\circ_{is})/RT} \tag{3-6a}$$

$$= K_i \tag{3-6b}$$

The equilibrium constant, K_i, is the solubility product constant. This may be seen by considering the limiting cases of the pure components and by noting that:

$$\lim_{x_i = 1} \sigma_i = 1. \tag{3-7}$$

The relationship between the solid and liquid at equilibrium for both species is written out in explicit form in Equation 3-8.

$$a_{Ca^{++}}\, a_{SO_3^=}\, a^{\frac{1}{2}}_{H_2O} = K_1 \sigma_1\, x_{CaSO_3 \cdot \frac{1}{2}H_2O} \tag{3-8a}$$

$$a_{Ca^{++}}\, a_{SO_4^=}\, a^{\frac{1}{2}}_{H_2O} = K_2 \sigma_2\, x_{CaSO_4 \cdot \frac{1}{2}H_2O} \tag{3-8b}$$

Dividing both sides of Equation 3-8b by the solubility product constant, K_2, gives Equation 3-9, the left-hand side of Equation 3-9 is, by definition, the relative saturation of $CaSO_4 \cdot \frac{1}{2}H_2$ in the liquid phase.

$$R.S._{CaSO_4 \cdot \frac{1}{2}H_2O} = \sigma_2\, x_{CaSO_4 \cdot \frac{1}{2}H_2O} \tag{3-9}$$

The mathematical form of the solid phase activity coefficient can be estimated from the empirical correlation of the liquid phase calcium sulfate relative saturation with the sulfate mole fraction in the corresponding solids. The relation given in Equation (3-10) gives the desired functional form to Equation (3-9),

$$\ln \sigma_{CaSO_4 \cdot \frac{1}{2}H_2O} = \alpha_1 + \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O} \qquad (3\text{-}10)$$

where the constants α_1 and α_2 are calculated from the experimental data.

Substituting this relationship for the activity coefficient into Equation (3-9) gives:

$$R.S._{CaSO_4 \cdot \frac{1}{2}H_2O} = x_{CaSO_4 \cdot \frac{1}{2}H_2O} \cdot \exp(\alpha_1 + \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O}) \qquad (3\text{-}12)$$

The mole fraction of sulfate in the solids can be calculated from Equation (3-12) given the relative saturation of calcium sulfate hemihydrate in the aqueous phase from which the solids are precipitated.

4.0 EXPERIMENTAL APPROACH

An experimental program was established to characterize the nature of the mechanism leading to coprecipitation of sulfate with $CaSO_3 \cdot \frac{1}{2}H_2O$. Controlled experimental conditions were used to first verify the existence of a coprecipitation product and then to measure the effects of solution composition. The precipitation rate and some measure of the sulfate concentration were the primary variables to be studied.

The experimental apparatus and sampling and analytical techniques used during this program are described in this section. Additional details are presented in Appendix C.

The experimental studies were divided into the following areas:

- selection and development of sampling and analytical methods which are consistent with the accurate measurement of sulfite and sulfate in both the liquid and solid phases,
- a series of experiments at low sulfite precipitation rates to establish whether or not a solid solution will precipitate from solutions near equilibrium,
- a series of experiments at higher precipitation rates to determine if kinetic effects are significant,
- investigation of the effects of:
  - dissolved magnesium
  - temperature
  - ionic strength (NaCl),
  - dissolving limestone and lime

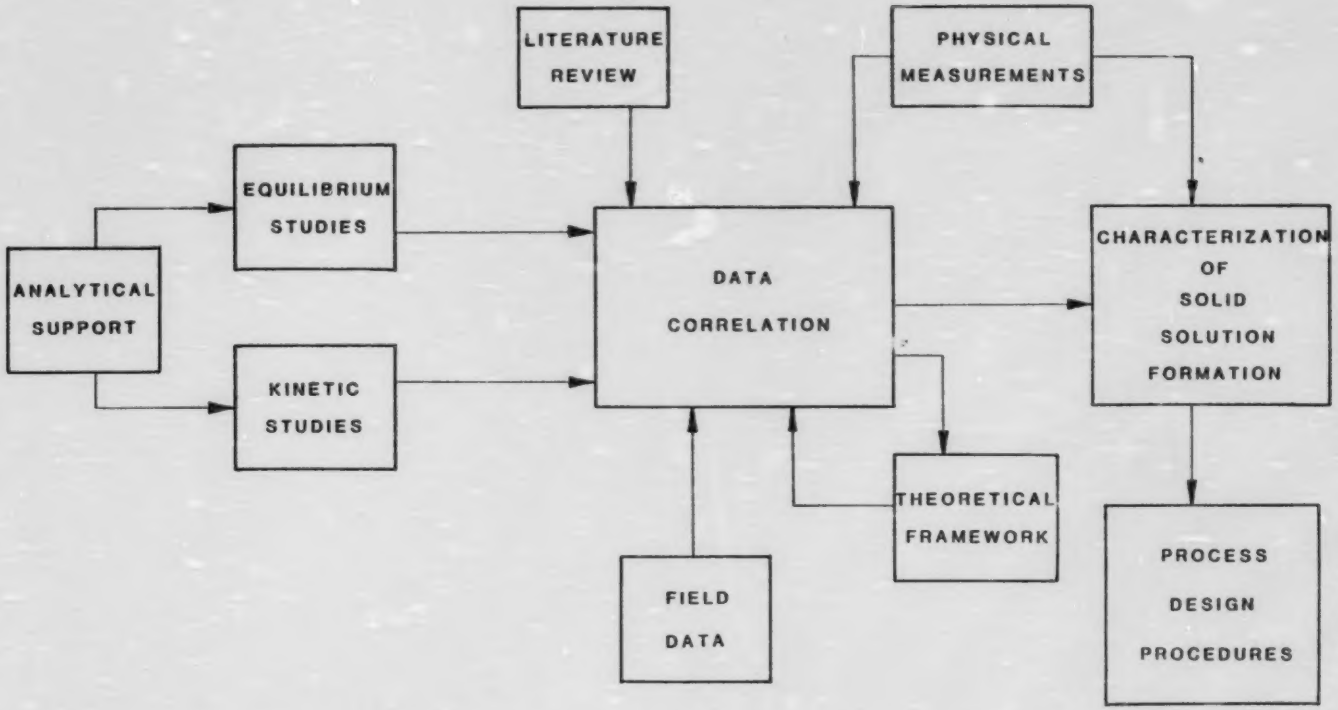


FIGURE 4-1. SCHEMATIC REPRESENTATION OF DATA ANALYSIS

This experimental approach in the equilibrium studies was terminated in the early phases of the test program due to the impracticality of long experimental run times (one to four weeks). Oxidation and other operational problems also prevented the practical application of this equilibrium approach over the required run times.

Equilibration Apparatus

This equipment, Figure 4-2, was designed to obtain equilibrium data from solids grown during the kinetics phase of this project. The solids were equilibrated with a liquor similar to that in which it was grown, thus allowing the relative influence of the equilibrium and kinetic effects on the sulfate content of the solids to be separated and quantified.

An experimental apparatus was designed and constructed to accommodate six experimental runs simultaneously at a controlled temperature in an inert atmosphere. A large plexiglas box was fabricated and served as the enclosure. Heat lamps connected to a temperature controller and thermistor system maintained the enclosure at a controlled temperature while two fans circulated nitrogen to minimize temperature gradients within the box. Thermometers suspended from the top of the box at several locations were used to monitor the temperature. Nitrogen entered the enclosure on the back side of the fans providing a constant oxygen purge of the enclosure.

Plexiglass cylinders with an internal volume of 570 ml were charged with appropriate solids and liquors. These solutions then were thoroughly mixed on a tumbling device designed especially for horizontal rotation of the cylinders at a constant

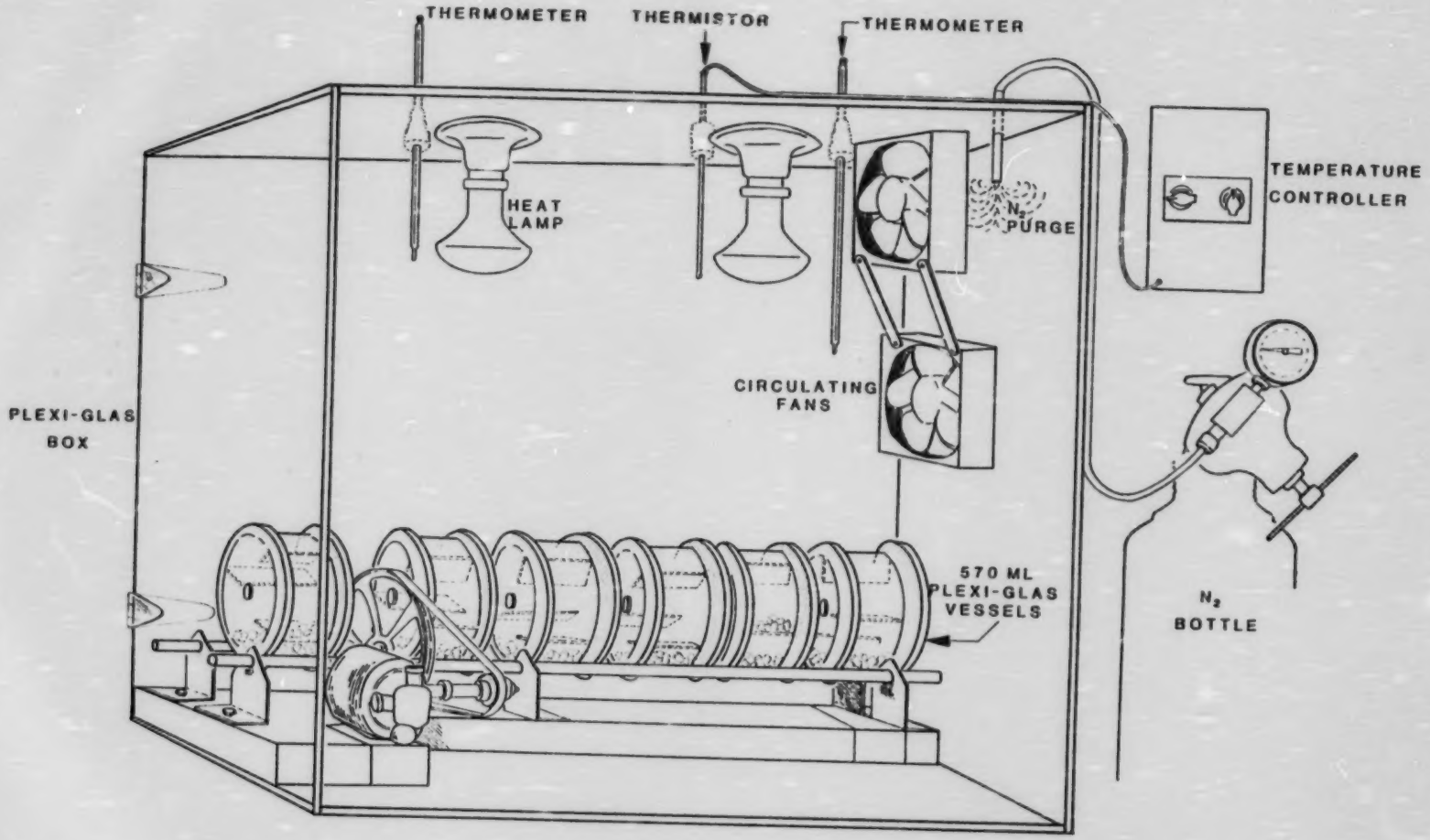


FIGURE 4-2. EQUILIBRIUM EXTRACTION APPARATUS

speed for long periods of time. Ceramic cylinders were used within the containers to produce grinding to expose new surfaces of the crystals for dissolution and precipitation. Additional details of this experimental technique are contained in Appendix C.

A sampling procedure was designed to ensure consistent and accurate measurements of sulfite and sulfate in both the liquid and solid phases. A pictorial representation of the sampling train utilized in these equilibrium studies is shown in Figure 4-3. Temperature and pH measurements of the equilibrated solutions were taken just prior to sample collection. Rapid liquid phase sampling to provide an aqueous sulfite sample and a diluted filtrate sample was accomplished by using a peristaltic pump and a 47 mm filter. All sampling lines were kept as short as possible and a constant purge of nitrogen was directed at the sample port in the vessel at all times during sampling to minimize any liquid contact with air. After collection of the two liquid samples, the equilibrated solids were obtained by filtration of the slurry. The filtration was done in a nitrogen atmosphere.

Kinetic Apparatus

The kinetic apparatus, shown in Figures 4-4 and 4-5, served as a precipitation device to quantify the influence of solution composition on the formation of the coprecipitate. With this flow-through system, experimental conditions such as temperature, calcium sulfite precipitation rate and relative saturation of calcium sulfate can all be varied independently to simulate the reactor compositions necessary for this study.

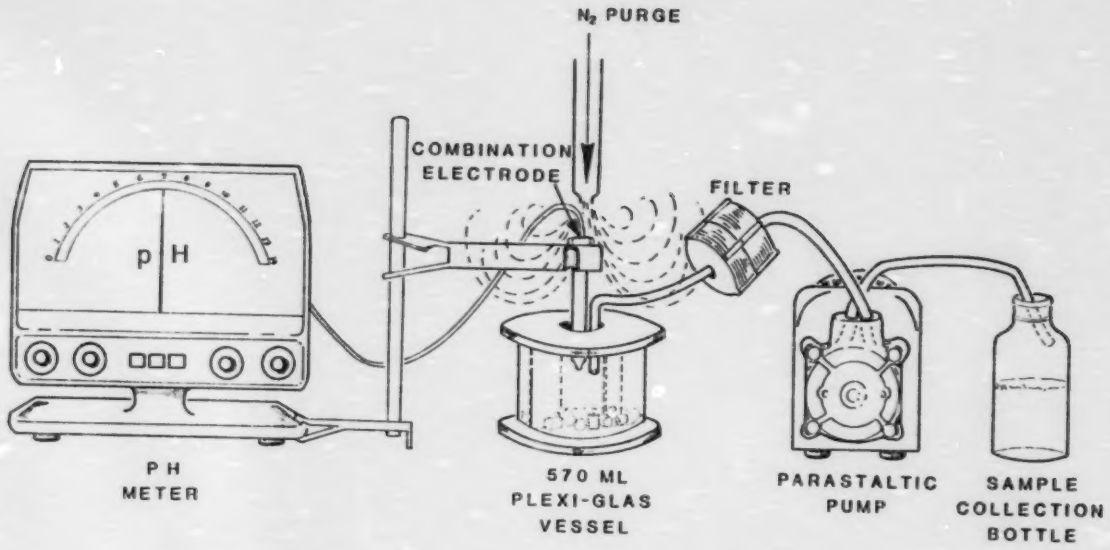


FIGURE 4-3. THE SAMPLING TRAIN UTILIZED IN EQUILIBRIUM STUDIES

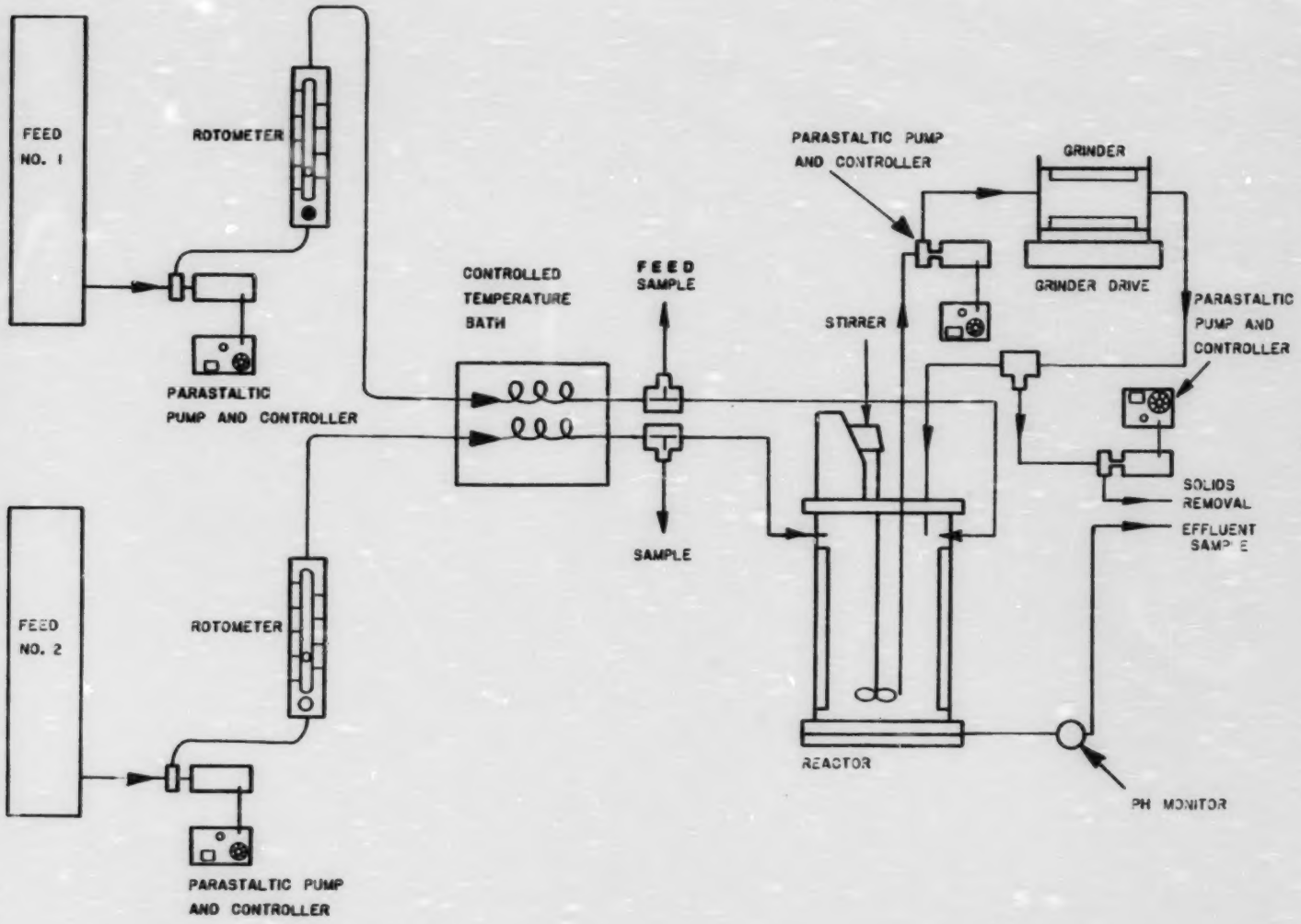


FIGURE 4-4. PRECIPITATION APPARATUS FOR KINETIC STUDIES

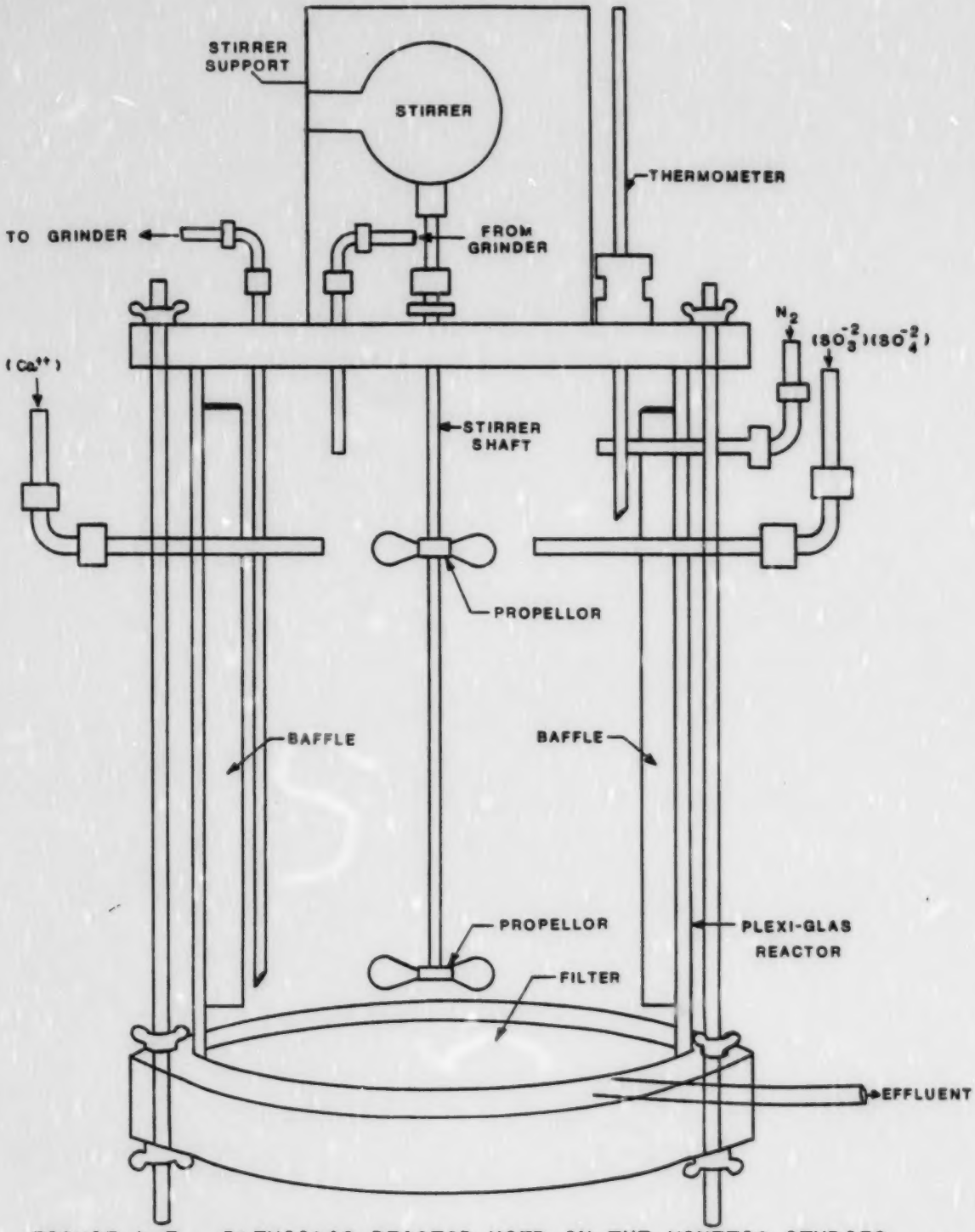


FIGURE 4-5. PLEXIGLAS REACTOR USED IN THE KINETIC STUDIES

The primary components of the kinetics apparatus are:

- a continuous liquid/slurry feed system,
- a reactor,
- a grinder,
- a continuous mixed product removal system and
- a pH monitor.

The continuous liquid/slurry feed system provided two well-defined feed streams to the reactor where precipitation occurred. A continuous mixed product removal system and grinder were incorporated into the kinetics apparatus in order to maintain a constant slurry density and particle size in the reactor. The pH of the reactor effluent was monitored in a flow-through cell immediately downstream of the filter.

Each component of the kinetics apparatus was periodically checked to ensure that consistent and accurate measurements of the individual test parameters were being maintained. Additional details of the kinetics apparatus are given in Appendix C.

4.2 Sampling Techniques Utilized in Kinetic Experiments

The sampling train and procedures were designed to obtain consistent and accurate measurements of the compositions of both the liquid and solid phases. All sampling lines and fittings were nalgon and teflon to minimize chemical changes in the samples. For the most part sampling provisions were incorporated in the experimental apparatus flow system (see Figure 4-4).

Feed stream samples were obtained by diverting the feed liquors through three-way stopcocks located in front of the reactor into prepared sample bottles. The reactor effluent liquor passed through the pH monitor and was collected for analysis. Precipitated solids were recovered from the reactor by filtering a portion of the slurry removal stream.

Sufficient samples were taken during each run to characterize the streams entering and leaving the reactor. Diluted filtrate samples were taken from the two feed streams and the reactor effluent after the line-out period of approximately three solids residence times. Aqueous sulfite samples were taken in a similar fashion and were used with the pH measurements to monitor the approach to steady state. Periodic slurry samples were taken and filtered to obtain the weight percent solids in the reactor. After the system had been operated for three solids residence times, the reactor solids were collected, washed and dried.

A sampling procedure was developed to minimize contamination during sampling of the solids from high magnesium sulfate liquid phase concentrations. Basically this technique consists of a rapid separation of the precipitated solids from the liquid phase. This separation was achieved with a pressurized filtering system using polycarbonate filter membranes. The solids are then twice slurried in a saturated calcium sulfite solution and filtered. Next the solids are rinsed with acetone and allowed to dry in an inert atmosphere. Detailed descriptions of this and other sampling techniques are included in Appendix C.

4.3 Analytical Technique

The analytical methods used during this program are breifly discussed in this section. A more detailed description of each procedure is included in Appendix D.

For the most part the analytical techniques used were those previously selected and modified by Radian for SO_2 scrubber slurry analyses. A more sensitive sulfate procedure for solids analysis was developed especially for this program.

Chemical Analysis of Liquid Phase Samples

Calcium, sodium and magnesium analyses on the filtered feed and reactor effluent streams were performed by atomic absorption spectroscopy. Liquid phase sulfite measurements were made using an iodometric back titration with sodium arsenite. The end point of the titration was determined amperimetrically.

Aqueous sulfate concentrations were measured by substracting the sulfite concentration from a total sulfate plus sulfite measurement. The latter value was obtained by first oxidizing the sulfite to sulfate and then measuring the resultant total sulfate. The sulfate analytical procedure consists of an initial cation exchange process followed by an evaporation step at 75°C. The resulting sulfuric acid is then titrated with a standard NaOH solution to determine the quantity present.

The chloride analyses of the aqueous samples were made using a potentiometric titration technique using a standardized silver nitrate solution as the titrant. Carbonate analyses were made by first acidifying the solution. A nitrogen sweep gas was then passed through the acidified solution. The CO_2 content of the sweep gas was measured with a nondispersive infrared analyzer.

Analytical Techniques for Solids Characterization

Both chemical and instrumental techniques were used to determine the chemical composition of the solids precipitated in the laboratory studies. These techniques were also applied to some solids field samples from lime- and limestone-based SO_2 scrubbing units. Specific chemical analyses of the solids were made to determine the calcium, sulfate and sulfite concentration. Magnesium, chloride and carbonate analyses of the solids were run periodically. Additional characterization of the solids was accomplished using such instrumental techniques as infrared spectroscopy, differential scanning colorimetry, X-ray diffraction and thermogravimetry.

The specific sulfate, sulfite and carbonate analyses were carried out directly on a portion of the sample. The remaining chemical species were determined subsequent to the dissolution of a portion of the sample. The solids were dissolved in an acidic peroxide solution. Aliquots of this solution were then analyzed for calcium, magnesium, sodium, chloride and total sulfur using the same procedures described for the liquid phase analyses.

A specific sulfate analytical procedure was developed during this program to accurately measure the sulfate concentrations in the precipitated solids. A weighed quantity of solid samples was dissolved in an oxygen-free acidic solution. CO_2 was bubbled through the solution to remove the sulfite as SO_2. Once the dissolution was complete the solution was removed and the sulfate level was determined by the ion-exchange, titrimetric sulfate method. This technique provided improved accuracy in the sulfate determinations over the concentration range encountered in coprecipitate solids.

The presence of large excesses of calcium carbonate with the coprecipitate solids tends to cause some error in this sulfate determination. This situation developed during some of the limestone slurry tests where low utilization was encountered.

Additional characterization of the solids was done using infrared spectroscopy (IR), differential scanning colorimetry (DSC), X-ray diffraction, and thermogravimetric analysis (TGA). Infrared spectroscopy was used to qualitatively and quantitatively measure the sulfate in the solid solution samples. The presence of gypsum in the solids was identified by IR, DSC or X-ray diffraction.

X-ray diffraction was used to measure the crystalline phases present in the precipitated solids. However, the diffraction patterns for the solid solution samples were indistinguishable from that of pure calcium sulfite hemihydrate.

The dehydration temperatures as well as the quantities of water lost from the solids were determined using DSC and TGA methods.

4.4 Experimental Calculations

This section contains a brief description of the calculations utilized in the data analysis of the experimental runs. Liquid phase calculations included computation of the activities of each of the ions and relative saturations of calcium sulfite hemihydrate and calcium sulfate hemihydrate and dihydrate by Radian's aqueous ionic equilibrium program. The calcium sulfite precipitation rate was calculated from inlet and effluent aqueous sulfite concentrations and flow rates.

Solid phase calculations included the determination of the sulfate and sulfite mole fractions of the precipitated product based on the chemical analysis of the solids. The sulfite precipitation rate was also calculated from the measured slurry removal rate, weight percent solids and the solids analysis. The sulfate precipitation rate was based on the sulfite precipitation rate and the sulfate to sulfite ratio in the solid. These rates were normalized by dividing by the mass of the seed crystals in the reactor.

Solid and liquid mass balances across the reactor were calculated to evaluate the reliability of the data collected for each experimental run. Total solid and liquor inlet molar rates were calculated and compared to total outlet solid and liquid molar rates. Agreement within expected experimental error of the total inlet and outlet mass rates supported the accuracy of the measured flowrates and chemical analyses. The calcium, sulfite, and sulfate precipitation rates based on liquid analyses were compared for consistency with the corresponding precipitation rates based on solids analyses. Detailed equations used in calculations are presented in Appendix C.

5.0 RESULTS

This section presents the results of the experimental studies designed to characterize the formation of the calcium sulfite/sulfate coprecipitation phenomenon. Results of the physical techniques used to identify, characterize and measure the solid solution are also presented. The qualitative and quantitative effects of the following variables on the solid solution composition were evaluated:

- relative saturation of calcium sulfate hemihydrate,
- calcium sulfite precipitation rate,
- lime and limestone slurries,
- magnesium concentration,
- temperature, and
- ionic strength or sodium chloride concentration.

The experimental results of these parameter studies were interpreted within the framework of the theoretical relations described previously. Namely, the activity product of the aqueous phase calcium sulfate was correlated to the sulfate content of the precipitated solids. The precipitation rate had no measurable effect on the amount of sulfate incorporated into the solids.

A summary of the analytical results as well as the calculated values for the experiments conducted during this program are presented in Tables 5-1, 5-2, 5-3, 5-4 and 5-5.

TABLE 5-1. LIQUID AND SOLID COMPOSITION DATA OF EXPERIMENTAL RUNS

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (mg/liter)							Solid Analyses (wt %)				
				Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$
7/02/75	E-5	6.72	46	652	78	N.D.	64	N.D.	46	1500	28.6	N.D.	N.D.	47.2	12.0
7/18/75	E-8	7.73	45	247	2	"	4	"	45	534	33.3	"	"	50.4	5.7
7/29/75	E-9	7.88	40	337	33	"	4	"	37	750	30.7	"	"	53.8	9.0
8/04/75	E-10	8.40	43	45	0	"	1	"	62	278	30.6	"	"	51.4	8.5
8/11/75	E-11	8.01	49	376	0	"	< 1	"	31	840	31.2	"	"	54.1	8.4
8/29/75	K-2	8.47	49	342	377	"	650	"	58	790	28.7	"	"	54.6	5.6
9/05/75	K-3	8.20	49	364	450	"	1410	"	51	810	29.3	"	"	57.0	2.6
9/12/75	K-6	8.20	50	356	400	"	630	"	51	730	29.8	"	"	55.7	3.6
9/16/75	K-8	8.11	49	508	640	"	910	"	49	1180	26.9	"	"	49.1	7.6
9/17/75	K-9	8.06	49	468	850	"	1320	"	54	1060	30.4	"	"	53.2	7.4
9/25/75	K-10	7.78	49	388	1190	"	1950	"	62	970	30.8	"	"	53.9	5.4
9/26/75	K-11	8.09	49	504	570	"	970	"	56	1080	29.2	"	"	51.2	6.2
9/29/75	K-12	8.12	50	480	580	"	890	"	53	1140	19.2	"	"	49.1	5.0
10/01/75	K-13	7.90	49	450	515	"	800	"	58	1120	26.8	"	"	48.5	4.1
10/03/75	K-14	8.48	49	46	136	"	149	"	86	20	26.9	"	"	58.4	0.5
10/20/75	K-15	8.80	46	45	127	"	146	"	100	12	27.4	"	"	58.5	0.5
10/22/75	K-16	8.18	46	552	880	"	1090	"	70	1370	27.5	"	"	51.8	5.9
10/23/75	K-17	8.08	48	636	680	"	1190	"	58	1380	29.2	"	"	49.1	6.6
10/27/75	K-18	8.08	48	796	470	"	1490	"	54	1140	29.4	"	"	50.0	6.9
10/28/75	K-19	8.00	48	692	780	"	1390	"	62	1540	28.3	"	"	47.6	7.3
10/29/75	K-20	7.90	49	684	750	"	1450	"	57	1660	26.1	"	"	45.1	6.3
11/03/75	K-21	8.30	49	696	730	"	1490	"	56	1500	28.5	"	"	48.5	6.5
11/04/75	K-22	8.57	50	512	92	2120	2220	"	242	5360	28.6	"	"	51.7	7.7
11/05/75	K-23	8.87	52	512	92	2220	2130	"	221	5190	27.6	"	"	52.2	3.6

(continued)

TABLE 5-1 (continued)

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (mg/liter)							Solid Analyses (wt %)				
				Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$
11/18/75	K-24	8.49	50	456	820	N.D.	1170	N.D.	285	1060	30.7	N.D.	N.D.	51.7	8.7
11/20/75	K-26	6.07	46	351	560	"	920	"	368	437	29.1	"	"	38.0	10.9
12/01/75	K-27	6.32	50	840	1910	"	3110	"	174	1260	27.4	"	"	7.4	49.9
12/01/75	K-28	7.90	47	1120	1360	"	3420	"	191	2440	27.1	"	"	25.7	10.7
12/01/75	K-29	6.81	50	656	1980	"	3300	"	1060	5700	30.7	"	"	16.9	41.1
12/02/75	K-30	6.11	50	492	2620	"	1210	86	690	3590	29.5	"	"	45.1	8.0
12/02/75	K-31	6.12	50	524	4230	"	940	85	660	6100	32.8	"	"	44.7	7.9
12/05/75	K-32	6.11	50	504	1790	"	2980	85	690	2580	29.4	"	"	25.7	7.9
12/05/75	K-33	5.90	49	1320	1290	"	3160	118	660	2510	34.5	"	"	21.7	10.0
12/08/75	K-34	6.00	50	1280	1080	"	2680	149	560	2180	35.1	"	"	21.6	5.9
12/08/75	K-35	6.12	51	704	2180	"	2700	118	530	1760	35.1	"	"	12.7	3.9
12/12/75	K-37	5.98	51	486	46000	10000	23400	73	6520	41000	29.0	<0.1	"	41.1	17.0
12/19/75	K-38	6.12	41	445	1180	N.D.	1160	N.D.	410	2070	29.1	N.D.	"	45.7	10.7
12/22/75	K-39	5.61	48	778	5240	13400	20900	"	4020	10900	28.6	<0.1	"	46.6	10.1
12/30/75	K-40	6.22	50	1170	2370	14800	20600	"	1870	11200	27.7	< .1	"	29.5	27.5
12/31/75	K-41	5.60	49	1060	6440	12600	22700	"	4520	22300	29.2	< .1	"	48.5	10.1
12/31/75	K-42	5.71	48	1130	3110	11700	18400	"	2860	24600	29.0	< .1	"	48.2	11.2
1/27/76	K-44	6.23	50	1030	1400	13600	27300	"	1370	19200	29.0	< .1	"	51.4	10.1
2/02/76	K-45	6.18	50	1110	1090	12900	29100	"	1190	19900	27.1	.4	"	12.2	42.1
2/03/76	K-46	6.28	49	990	920	6100	13500	"	820	11300	28.5	< .1	"	50.6	10.4
2/03/76	K-47	6.20	50	910	1040	8500	22300	"	1030	10100	28.5	< .1	"	51.1	10.1
2/04/76	K-48	6.24	51	1230	910	12600	31200	"	830	8200	28.2	.2	"	47.8	11.1
2/10/76	K-49	6.21	50	1180	1020	12200	30200	"	615	8930	29.8	< .1	"	50.4	9.1
2/17/76	K-50	7.95	40	381	930	N.D.	1510	"	157	750	29.5	N.D.	"	56.0	7.0
2/17/76	K-51	8.70	41	161	740	"	1450	"	147	830	29.4	"	"	53.6	6.6
2/17/76	K-52	8.11	49	160	980	"	1440	"	177	760	30.1	"	"	51.0	7.7
2/17/76	K-53	8.30	61	277	1000	"	1400	"	115	930	29.7	"	"	53.6	8.1

(continued)

TABLE 5-1 (continued)

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (mg/liter)						Solid Analyses (wt %)					
				Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$
2/24/76	K-56	8.28	41	590	970	N.D.	1570	N.D.	166	840	29.6	N.D.	N.D.	51.8	6.0
3/10/76	K-59	6.25	54	317	892	"	N.D.	310	740	1380	16.0	"	"	17.0	1.1
3/11/76	K-60	5.70	55	169	1050	"	"	650	1510	1380	10.2	"	"	44.0	5.0
3/19/76	K-61	5.70	56	168	1620	"	"	560	1640	2280	14.5	"	"	42.4	1.6
3/25/76	K-62	5.69	55	432	2940	"	"	N.D.	2620	5070	15.8	"	"	41.9	8.5
3/29/76	K-63	5.70	55	597	2510	"	"	"	1550	5900	N.D.	"	"	16.1	5.1
3/31/76	K-63B	5.70	55	505	12600	19000	"	"	7800	97000	"	"	"	42.7	4.6
*4/02/76	K-64	5.93	53	577	11600	N.D.	27800	310	3100	27700	15.5	"	"	14.1	0.96
*4/05/76	K-65	5.80	55	311	7100	14000	N.D.	280	12400	67000	19.5	"	"	9.1	0.48
*4/05/76	K-66	5.89	58	281	7200	13700	"	210	11800	62000	15.8	"	"	7.6	0.48
*4/06/76	K-67	5.79	43	280	7600	10600	"	320	12700	50600	17.8	"	"	1.8	0.14
*4/08/76	K-68	5.67	51	312	6800	9800	"	280	7400	43000	14.1	"	"	6.7	0.61
4/22/76	K-69	7.91	50	173	600	N.D.	1360	N.D.	56	197	30.7	"	"	56.2	4.6
4/22/76	K-70	8.12	52	144	1030	"	1350	"	58	910	10.5	"	"	51.0	7.9
4/22/76	K-71	6.87	53	405	1000	"	1490	15	179	870	29.9	"	0.72	52.5	8.1

N.D. - Not determined.

* The limestone content of the solids is so high that the solid sulfate analyses are inaccurate.

TABLE 5-2. SUMMARY OF MOLAR COMPOSITION OF LIQUID AND SOLID PHASES OF ALL EXPERIMENTAL RUNS

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (moles/liter)							Solid Analyses (moles/gram)					
				Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	T.S.	$SO_3^{=}$	$SO_4^{=}$
7/03/75	E-5	6.72	46	16.1	3.4	N.D.	1.8	N.D.	0.58	15.6	7.15	N.D.	N.D.	7.15	5.90	1.25
7/18/75	E-8	7.71	45	6.18	0.1	"	.1	"	.56	5.56	8.11	"	"	7.06	6.30	.59
7/29/75	E-9	7.88	40	8.79	1.4	"	.11	"	.46	7.76	7.68	"	"	5.97	6.72	.94
8/04/75	E-10	8.40	41	1.12	0.	"	.03	"	.77	.29	7.65	"	"	7.57	7.52	.05
8/11/75	E-11	8.01	49	9.4	0.	"	.02	"	.19	8.70	7.79	"	"	7.14	6.61	.88
8/29/75	K-2	8.47	49	8.56	16.4	"	18.2	"	.72	8.2	7.17	"	"	7.41	6.82	.58
9/05/75	K-3	8.20	49	9.10	19.4	"	39.6	"	.64	8.4	7.31	"	"	7.40	7.13	.27
9/12/75	K-6	8.20	50	8.9	17.4	"	17.6	"	.64	7.6	7.46	"	"	7.33	6.96	.37
9/16/75	K-8	8.11	49	12.7	27.6	"	25.6	"	.61	12.3	6.71	"	"	6.91	6.14	.79
9/17/75	K-9	8.06	49	11.7	16.8	"	17.2	"	.67	11.0	7.60	"	"	7.42	6.65	.77
9/25/75	K-10	7.78	49	9.7	51.6	"	54.8	"	.77	10.1	7.71	"	"	7.42	6.74	.56
9/26/75	K-11	8.09	49	12.6	24.8	"	27.4	"	.70	11.3	7.10	"	"	7.01	6.40	.65
9/29/75	K-12	8.12	50	12.0	25.2	"	25.0	"	.66	11.9	4.80	"	"	4.57	6.14	.52
10/01/75	K-13	7.90	49	11.3	24.4	"	22.4	"	.72	11.7	6.71	"	"	6.70	6.06	.43
10/03/75	K-14	8.48	49	1.15	5.9	"	4.20	"	1.07	.21	6.72	"	"	6.79	7.30	.05
10/20/75	K-15	8.8	46	1.13	5.5	"	4.10	"	1.25	.13	6.86	"	"	7.25	7.31	.05
10/22/75	K-16	8.18	47	13.8	38.2	"	30.8	"	.87	14.1	6.87	"	"	7.17	6.48	.61
10/23/75	K-17	8.08	48	15.9	29.6	"	33.6	"	.72	14.4	7.30	"	"	6.94	6.16	.69
10/27/75	K-18	8.08	48	19.9	20.4	"	42.0	"	.67	11.9	7.36	"	"	7.13	6.25	.77
10/28/75	K-19	8.00	48	17.3	36.0	"	39.2	"	.78	16.0	7.08	"	"	7.04	5.95	.76
10/29/75	K-20	7.90	49	17.1	32.6	"	40.9	"	.71	17.1	6.52	"	"	7.11	5.64	.66
11/03/75	K-21	8.30	49	17.4	31.8	"	42.	"	.70	15.6	7.11	"	"	7.10	6.06	.68
11/04/75	K-22	8.57	50	12.8	4.0	87.2	62.4	"	3.02	55.8	7.14	"	"	7.01	6.71	.23
11/05/75	K-23	8.87	52	12.8	4.0	91.5	60.2	"	2.76	56.1	6.91	"	"	7.14	6.52	.37

(continued)

TABLE 5-2 (continued)

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (moles/liter) Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Solid Analyses (moles/gram) Ca^{++}	Mg^{++}	$CO_3^{=}$	T.S.	$SO_3^{=}$	$SO_4^{=}$
11/18/75	K-24	8.49	50	11.4	35.8	N.D.	33.0	N.D.	1.49	11.1	7.56	N.D.	N.D.	6.71	6.46	0.91
11/20/75	K-26	6.07	46	8.83	24.4	"	26.0	"	1.56	4.55	7.27	"	"	6.75	4.75	1.13
12/01/75	K-27	6.32	50	21.0	83.0	"	87.6	"	4.60	14.0	6.86	"	"	5.15	0.92	5.20
12/01/75	K-28	7.90	47	28.0	146.	"	96.4	"	2.17	25.5	6.84	"	"	6.31	1.21	3.15
12/01/75	K-29	6.81	50	16.4	173.	"	93.0	"	2.41	59.4	6.78	"	"	5.99	2.11	4.10
12/02/75	K-30	6.11	50	12.3	114.	"	34.0	1.43	13.3	37.4	7.55	"	"	5.67	5.64	.83
12/02/75	K-31	6.12	50	13.1	184.	"	76.5	1.41	10.1	63.5	7.38	"	"	N.D.	5.59	.82
12/05/75	K-32	6.11	50	12.6	78.	"	83.9	1.41	8.6	26.9	8.20	"	"	3.47	3.15	.80
12/05/75	K-33	5.90	50	33.0	56.2	"	88.4	1.96	8.3	26.1	7.36	"	"	3.63	2.96	1.04
12/08/75	K-34	6.00	49	12.0	46.8	"	75.4	2.48	7.0	24.8	8.62	"	"	3.44	2.70	.61
12/08/75	K-35	6.12	50	17.6	94.8	"	76.03	1.96	6.6	39.2	8.77	"	"	1.00	1.52	.41
12/12/75	K-37	5.98	51	12.1	2000.	408	656.	1.21	81.5	427.	7.25	0.07	"	6.24	5.39	1.25
12/19/75	K-38	6.32	41	11.1	60.	N.D.	32.6	N.D.	5.12	21.6	7.3	N.D.	"	6.75	5.65	1.11
12/22/75	K-39	5.61	48	19.4	228.	549	594.	"	50.2	122.	7.15	0.025	"	6.70	5.81	1.05
12/30/75	K-40	6.22	50	29.2	101.	612	579.	"	23.4	325.	6.81	.025	"	6.36	3.69	2.86
12/31/75	K-41	5.60	49	25.9	280.	517	639.	"	54.6	232.	7.29	.052	"	6.99	6.06	1.08
12/31/75	K-42	5.73	48	28.3	135.	481	518.	"	35.7	257.	7.25	.022	"	7.20	6.02	1.17
1/02/76	K-44	6.23	50	25.7	60.7	560	766.	"	17.1	200.	7.24	.035	"	7.02	6.43	1.07
2/02/76	K-45	6.18	50	27.7	48.	529	817	"	14.9	207.	5.58	.18	"	5.60	1.52	4.40
2/03/76	K-46	6.28	49	24.6	40.	248	384.	"	10.3	118.	7.12	.02	"	7.22	6.33	1.08
2/03/76	K-47	6.20	50	22.7	45.4	354	634.	"	12.9	101.	7.32	.03	"	7.27	6.44	1.07
2/04/76	K-48	6.24	51	30.8	40.	520	880.	"	10.3	85.4	7.06	.07	"	6.98	5.97	1.16
2/10/76	K-49	6.21	50	25.9	44.4	500	853.	"	7.69	91.	7.45	.05	"	6.95	6.30	.95
2/17/76	K-50	7.95	40	9.53	40.4	N.D.	43.3	"	1.90	7.8	7.16	N.D.	"	N.D.	7.00	.73
2/17/76	K-51	8.70	41	9.02	41.0	"	41.0	"	1.84	8.66	7.34	"	"	"	6.70	.69
2/17/76	K-52	8.11	49	9.01	42.8	"	40.6	"	1.59	7.90	7.51	"	"	"	6.62	.80
2/17/76	K-53	8.30	61	6.92	41.6	"	39.6	"	1.44	9.66	7.40	"	"	"	6.69	.84

(continued)

TABLE 5-2 (continued)

Date	Run Number	pH	Temp. (°C)	Effluent Liquid Analyses (moles/liter) Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Solid Analyses (moles/gram) Ca^{++}	Mg^{++}	$CO_3^{=}$	T.S.	$SO_3^{=}$	$SO_4^{=}$
2/24/76	K-56	8.28	41	14.7	42.	N.D.	44.2	N.D.	2.08	8.76	7.39	N.D.	N.D.	N.D.	6.72	0.67
3/10/76	K-59	6.25	54	7.26	38.8	"	N.D.	5.2	9.26	14.4	8.98	"	"	"	1.5	.14
3/11/76	K-60	5.70	55	4.24	45.6	"	"	10.8	18.9	14.4	7.54	"	"	"	5.58	.52
3/19/76	K-61	5.70	56	4.20	70.4	"	"	9.4	20.5	23.7	8.61	"	"	"	5.30	.37
3/25/76	K-62	5.69	55	10.78	128.	"	"	N.D.	32.8	52.8	8.94	"	"	"	5.24	.89
3/29/76	K-63	5.70	55	14.9	110.	"	"	"	19.4	61.2	N.D.	"	"	"	2.04	.53
3/31/76	K-63B	5.70	55	12.6	568.	782	"	"	97.	1010.	"	"	"	"	5.34	.48
*4/02/76	K-64	5.93	53	13.8	1420.	N.D.	784.	5.2	38.7	290.	8.86	"	"	"	1.79	.10
*4/05/76	K-65	5.80	55	7.75	310.	574	N.D.	4.7	155.	700.	9.88	"	"	"	1.17	.05
*4/05/76	K-66	5.89	58	7.0	312.	516	"	3.5	148.	647.	8.94	"	"	"	.95	.05
*4/06/76	K-67	5.79	43	6.98	332.	436	"	5.4	159.	527.	9.43	"	"	"	.47	.035
*4/08/76	K-68	5.67	51	7.79	296.	404	"	4.7	92.	448.	8.52	"	"	"	.852	.064
4/27/76	K-69	7.91	50	9.3	76.	N.D.	38.4	N.D.	.70	2.06	7.68	"	"	7.47	7.02	.48
4/27/76	K-70	8.12	52	8.59	44.6	"	38.2	"	.73	9.67	7.61	"	"	7.41	6.62	.83
4/27/76	K-71	6.87	53	10.1	43.6	"	42.	.251	2.24	9.06	7.46	"	0.17	7.22	6.56	.87

N.D. - Not determined.

* The solids are so high in limestone that solid sulfate analyses are inaccurate.

TABLE 5-3. SUMMARY OF CALCULATED DATA FOR ALL EXPERIMENTAL RUNS

Date	Run Number	Liquor Type[1]	pH	Temp. (°C)	$a_{Ca^{++}}$ (10^{-3})	$a_{SO_3^=}$ (10^{-6})	$a_{SO_4^=}$ (10^{-3})	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	$SO_4^=$ Mole Fraction	Wt % Solid	Sulfite Precipitation Rate (mmole/g-min)	Initial Solids[2] τ, T/T
7/03/75	E-5	C.L.	6.72	46	4.86	0.25	4.26	1.76	0.92	0.41	0.17	0.0	0.0015	----
7/18/75	E-8	C.L.	7.73	45	2.49	.56	2.30	1.93	.25	.11	.09	.021	.0035	----
7/29/75	E-9	C.L.	7.88	40	3.15	.39	2.91	1.70	.51	.18	.13	.0	.0051	----
8/04/75	E-10	C.L.	8.40	43	0.52	2.55	0.20	1.90	.01	.004	.01	.010	.0072	----
8/11/75	E-11	C.L.	8.01	49	1.38	.29	1.04	1.44	.48	.21	.12	.006	.0010	----
8/29/75	K-2	C.L.	8.47	49	2.75	.62	2.56	2.54	.32	.14	.10	.074	.085	0.27
9/05/75	K-3	C.L.	8.20	49	1.00	.52	2.54	2.30	.34	.15	.07	.077	.046	.45
9/12/75	K-6	C.L.	8.20	50	2.99	.52	2.32	2.28	.31	.14	.06	.150	.057	.26
9/16/75	K-8	C.L.	8.11	49	1.80	.40	2.97	2.29	.52	.21	.13	.144	.046	.28
9/17/75	K-9	C.L.	8.06	49	4.06	.40	2.55	2.35	.45	.20	.14	.625	.064	.27
9/25/75	K-10	C.L.	7.78	49	2.80	.60	2.45	2.63	.32	.14	.08	1.28	.087	.03
9/26/75	K-11	C.L.	8.09	49	1.78	.46	2.95	2.58	.50	.22	.14	.088	0.57	.11
9/29/75	K-12	C.L.	8.12	50	1.57	.46	3.17	2.45	.51	.23	.13	.053	.062	.13
10/01/75	K-13	C.L.	7.90	49	1.16	.52	3.21	2.59	.48	.21	.10	.036	.051	.27
10/03/75	K-14	C.L.	8.48	49	0.43	3.60	0.13	2.29	.01	.003	.01	.062	.064	.20
10/20/75	K-15	C.L.	8.80	46	0.18	4.58	0.08	2.54	.0	.0	.01	.082	.047	.18
10/22/75	K-16	C.L.	8.18	47	1.83	.58	3.49	3.22	.60	.25	.10	.087	.050	.15
10/23/75	K-17	C.L.	8.08	48	4.48	.41	3.39	2.72	.68	.29	.11	.071	.032	.08
10/27/75	K-18	C.L.	8.08	48	6.01	.30	2.54	2.65	.68	.29	.13	.085	.056	.11
10/28/75	K-19	C.L.	8.00	48	4.71	.43	3.59	2.93	.75	.32	.12	.071	.041	.04
10/29/75	K-20	C.L.	7.90	49	4.51	.40	3.91	2.66	.80	.35	.11	.06	.028	.06
11/1/75	K-21	C.L.	8.30	49	4.75	.18	3.46	2.66	.74	.31	.12	.047	.048	.14
11/4/75	K-22	C.L.	8.57	50	2.72	.91	3.92	3.77	.48	.22	.16	.066	.020	.21
11/5/75	K-23	C.L.	8.85	52	2.71	.81	3.70	3.35	.46	.22	.12	.064	.012	.48

(continued)

TABLE 5-3 (continued)

Date	Run Number	Liquor Type[1]	pH	Temp. (°C)	$a_{Ca^{++}}$ (10^{-1})	$a_{SO_3^=}$ (10^{-5})	$a_{SO_4^=}$ (10^{-3})	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	$SO_4^=$ Mole Fraction	Wt % Solid	Sulfite Precipitation Rate (mole/g-min)	Initial Solids[2] τ
11/18/75	K-24	L.	8.49	50	1.16	1.13	2.88	5.33	0.42	0.19	0.15	0.107	0.18	0.20
11/20/75	K-26	L.	6.07	46	1.09	1.01	1.36	4.52	.19	.08	.23	.059	.15	.17
12/01/75	K-27	L.	6.32	50	1.96	1.45	5.95	8.52	1.06	.48	.85	.200	.17	.01
12/01/75	K-28	L.	7.90	47	5.79	0.98	5.09	8.23	1.30	.55	.49	.225	.67	.01
12/01/75	K-29	L.	6.81	50	2.56	1.38	8.72	5.55	1.00	.45	.67	.210	.21	.05
12/02/75	K-30	L.S.	6.11	50	2.04	2.80	7.18	5.50	.66	.30	.13	.018	.18	.01
12/02/75	K-31	L.S.	6.12	50	1.90	2.11	9.74	5.96	.84	.38	.13	.010	1.71	.01
12/05/75	K-32	L.S.	6.11	50	1.50	1.61	5.47	8.41	.86	.39	.20	.042	.213	.01
12/05/75	K-33	L.S.	5.90	50	2.04	1.25	4.36	13.1	1.39	.63	.26	.059	.117	.01
12/08/75	K-34	L.S.	6.00	49	2.10	1.22	4.47	12.9	1.34	.59	.19	.080	.114	.01
12/08/75	K-35	L.S.	6.12	50	3.02	1.74	7.11	7.80	.97	.44	.21	.067	.118	.01
12/12/75	K-37	L.S.	5.98	51	1.86	5.1	9.87	14.0	.75	.34	.19	.080	.114	.01
12/19/75	K-38	L.	6.32	41	2.40	2.26	5.31	7.54	.53	.19	.16	.065	.095	.01
12/22/75	K-39	L.	5.61	48	2.93	2.3	6.47	9.9	.85	.36	.16	.38	.130	.01
12/30/75	K-40	L.	6.22	50	4.66	1.4	7.94	9.8	1.60	.72	.44	.38	.068	.01
12/31/75	K-41	L.	5.60	49	4.29	2.4	5.94	14.9	1.08	.47	.15	.35	.030	.015
12/31/75	K-42	L.	5.73	48	4.34	2.1	7.53	13.3	.74	.32	.16	.18	.142	.01
1/27/76	K-44	L.	6.23	50	4.57	1.10	5.13	7.4	1.01	.46	.14	.29	.061	.15
2/02/76	K-45	L.	6.18	50	4.97	0.91	5.4	6.7	1.15	.52	.80	.22	.028	.06
2/03/76	K-46	L.	6.28	49	4.04	1.13	5.37	6.7	.96	.43	.15	.12	.175	.01
2/03/76	K-47	L.	6.20	50	4.14	1.02	3.16	6.2	.61	.26	.15	.19	.062	.07
2/04/76	K-48	L.	6.24	51	6.64	0.55	1.88	5.4	.54	.25	.16	.16	.021	.05
2/05/76	K-49	L.	6.21	50	5.25	0.43	1.28	3.19	.87	.39	.15	.20	.022	.24
2/17/76	K-50	C.L.	7.95	40	2.75	1.72	2.15	6.6	.25	.09	.09	.10	1.22	.01
2/17/76	K-51	C.L.	8.70	41	2.55	1.79	2.43	6.4	.26	.10	.09	.10	.65	.01
2/17/76	K-52	C.L.	8.11	49	2.59	1.40	2.12	5.4	.25	.11	.11	.10	.66	.01
2/17/76	K-53	C.L.	8.30	61	1.76	1.53	2.62	4.3	.21	.11	.11	.13	.53	.01

(continued)

TABLE 5-3 (continued)

Date	Run Number	Liquor Type	pH	Temp. (°C)	$a_{Ca^{++}}$ (10^{-3})	$a_{SO_3^=}$ (10^{-6})	$a_{SO_4^=}$ (10^{-3})	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	$SO_4^=$ Mole Fraction	Wt % Solid	Sulfite Precipitation Rate (mmole/g-min)	Initial Solids[2] $e^{-T/\tau}$
2/24/76	K-56	C.L.	8.28	41	4.30	1.32	2.11	7.9	0.39	0.14	0.09	0.12	0.52	0.07
3/10/76	K-59	L.S.	6.25	54	1.52	3.4	4.5	8.0	.32	.16	.18	.31	.130	.58
3/11/76	K-60	L.S.	5.70	55	.74	2.7	4.7	3.1	.17	.085	.12	.19	.090	.07
3/19/76	K-61	L.S.	5.70	56	.49	2.9	10.9	2.16	.24	.175	.08	.17	.093	.13
3/25/76	K-62	L.S.	5.69	55	1.26	1.9	8.1	7.46	.49	.24	.17	.40	.116	.19
3/29/76	K-63	L.S.	5.70	55	1.80	2.2	11.0	6.10	.93	.46	.24	.05	.069	.17
3/31/76	K-63B	L.S.	5.70	55	1.10	3.0	28.0	5.07	1.17	.68	.09	.60	.119	.11
*4/02/76	K-64	L.S.	5.93	53	1.47	4.6	13.3	10.1	.84	.40	.09	.30	.083	.11
*4/05/76	K-65	L.S.	5.80	55	.57	6.7	24.6	5.8	.63	.31	.05	.51	.221	.03
*4/05/76	K-66	L.S.	5.89	58	.49	7.4	23.8	5.7	.55	.29	.05	.45	.290	.08
*4/06/76	K-67	L.S.	5.79	43	.51	10.5	23.9	7.5	.50	.19	.03	.31	.332	.04
*4/08/76	K-68	L.S.	5.67	51	.66	4.2	19.9	4.1	.58	.27	.04	.16	.083	.06
4/27/76	K-69	C.L.	7.91	50	3.62	.45	.56	2.4	.09	.04	.06	.19	.272	< .01
4/27/76	K-70	C.L.	8.12	52	2.54	.59	2.5	2.3	.30	.14	.11	.094	.471	< .01
4/17/76	K-71	C.L.	6.87	53	2.79	1.1	2.1	5.3	.30	.14	.12	.085	.487	< .01

1. Three types of liquors were used to study the formation of the solid solution: C.L. - clear liquor containing an initial calcium sulfite seed charge; L. - lime slurry containing an initial calcium sulfite seed charge; and L.S. - limestone slurry containing an initial calcium sulfite seed charge.

2. $e^{-T/\tau}$ is the mathematical equation expressing the fraction of initial $CaSO_3 \cdot \frac{1}{2}H_2O$ seed present in the reactor solids at the end of the run.

* The limestone content of the solids is so high that the solid sulfate analyses are inaccurate.

TABLE 5-4. LIQUID AND SOLID COMPOSITION DATA FOR EQUILIBRATION RUNS

Date	Run No.	pH	Temp. (°C)	Liquid Analyses (mg/liter) Ca^{++}	Na^{+}	Mg^{++}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	Solid Analyses (wt %) Ca^{++}	Mg^{++}	$SO_3^{=}$	$SO_4^{=}$
1/16/76 - 2/21/76	Q-1	7.29	50.0	520	460	0	750	26.9	1,250	28.4	0	54.8	7.1
" "	Q-2	7.30	50.0	530	470	0	760	25.9	1,260	29.5	0	55.1	2.4
" "	Q-3	7.38	50.0	500	470	0	770	29.5	1,180	29.1	0	52.4	7.5
" "	Q-4	7.31	50.0	690	74	4	1,160	31.4	1,680.	29.4	0	49.8	10.1
" "	Q-5	7.31	50.0	670	740	4	1,150	32.5	1,640	29.2	0	50.0	10.8
" "	Q-6	7.38	50.0	690	750	0	1,160	25.4	1,700	26.5	0	48.7	7.0
1/31/76 - 2/11/76	Q-7	7.51	49.1	46	14	0	0	[illegible].6	45	30.2	0	59.1	0.6
" "	Q-8	7.08	50.0	460	510	0	730	25.8	1,060	29.8	0	58.4	1.0
" "	Q-9	7.20	49.0	670	---	10,200	21,500	258.	13,700	29.7	0	58.4	0.6
" "	Q-10	7.11	48.9	950	---	11,600	23,200	289.	18,600	27.4	0.2	46.4	10.1
" "	Q-11	7.13	48.7	930	---	11,600	23,400	284.	18,100	28.8	0.1	50.1	8.8
" "	Q-12	6.95	48.0	930	---	11,700	23,200	287.	18,600	28.4	0.1	50.6	9.0
3/10/76 - 4/07/76	Q-13	6.80	52.0	453	471	0	780	32.8	1,080	27.2	---	62.8	0.
" "	Q-14	7.27	52.1	453	508	0	762	30.4	1,070	17.4	---	19.1	0.
3/24/76 - 4/07/76	Q-15	6.22	52.0	465	485	0	815	48.0	1,100	23.4	---	51.8	7.6
" "	Q-16	6.81	51.7	501	464	0	734	33.6	1,120	23.7	---	45.8	8.8
" "	Q-17	7.20	52.1	461	480	0	808	24.0	1,110	18.7	---	40.1	8.1
" "	Q-18	6.50	52.0	513	441	0	826	58.4	1,200	15.6	---	32.6	1.7

TABLE 5-5. SUMMARY OF RESULTS OF EQUILIBRIUM RUNS Q-1 THROUGH Q-18

Duration of Equil. (Hours)	Run No.	Kinetic Number	Mode*	pH	Temp. (°C)	Equilibrium Relative Saturation			Original Mole Fraction		Equilibrium Mole Fraction	
						$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$SO_3^=$	$SO_4^=$	$SO_3^=$	$SO_4^=$
120	Q-1	K-9	G	7.29	50	1.15	0.27	0.60	0.86	0.14	0.97	0.03
120	Q-2	K-9	NG	7.30	50	1.12	.27	.61	.86	.14	.96	.04
120	Q-3	K-38	G	7.38	50	1.28	.27	.60	.84	.16	.89	.11
120	Q-4	K-41	G	7.31	50	1.38	.17	.82	.85	.15	.86	.14
120	Q-5	K-41	NG	7.31	50	1.43	.35	.78	.85	.15	.85	.15
120	Q-6	K-19,20	G	7.38	50	1.13	.17	.82	.88	.12	.89	.11
264	Q-7	$CaSO_3 \cdot \frac{1}{2}H_2O$	G	7.51	49.1	1.20	.004	.009	1.00	.00	.99	.01
264	Q-8	$CaSO_3 \cdot \frac{1}{2}H_2O$	G	7.08	50	1.00	.22	.49	1.00	.00	.99	.01
264	Q-9	$CaSO_3 \cdot \frac{1}{2}H_2O$	G	7.20	49	1.27	.25	.57	1.00	.00	.99	.01
264	Q-10	K-41	G	7.11	48.9	1.78	.41	.58	.85	.15	.85	.15
264	Q-11	K-44	G	7.13	48.7	1.72	.41	.94	.86	.14	.87	.13
264	Q-12	K-44	G	6.95	48.0	1.70	.41	.96	.86	.14	.87	.13
648	Q-13	$CaSO_3 \cdot \frac{1}{2}H_2O$	G	7.20	52.3	0.93	.24	.56	1.00	.00	1.00	.00
648	Q-14	$CaSO_3 \cdot \frac{1}{2}H_2O$	G-15	6.50	52.0	1.54	.27	.61	1.00	.00	1.00	.00
312	Q-15	$CaSO_3 \cdot \frac{1}{2}H_2O$	G-15	6.30	52.0	1.06	.23	.54	1.00	.00	.96	.04
312	Q-16	K-41	G-15	7.27	52.1	1.20	.23	.51	.85	.15	.86	.14
312	Q-17	$CaSO_3 \cdot \frac{1}{2}H_2O$	G-30	6.27	52.0	.89	.24	.55	1.00	.00		
312	Q-18	K-41	G-30	7.27	51.7	1.14	.26	.59	.85	.15		

* G - Grinding mode assumed with three balls unless noted otherwise, e.g., G-30 is grinding with 30 ball charge.
NG - No grinding.

The operating conditions for each test are included in Tables 5-1 and 5-2 with the steady-state liquid and solid analyses. The aqueous compositions are given in milligrams per liter in Table 5-1 and in millimoles per liter in Table 5-2.

The computer calculated activities and relative saturations of the pertinent aqueous constituents are given in Table 5-3. The weight percent suspended solids, calcium sulfite precipitation rate and the dilution fraction of the product solids are also included in this table.

Experimental results obtained in the equilibration studies are presented in Tables 5-4 and 5-5. The duration of equilibration of precipitated solids with their mother liquor is given in minutes. The original sulfite and sulfate mole fractions of the solids before equilibration are reported as are the mole fractions after equilibration.

5.1 Physical Characterization of the Calcium Sulfite-Sulfate Solid Solution

5.1.1 Qualitative Application of Infrared Spectral Analysis

Infrared spectroscopy was successfully used to confirm the presence of sulfate in the calcium sulfite solids. The infrared absorption due to the sulfate ion showed that the incorporation occurred by the substitution of a sulfate ion for a sulfite ion in the crystal lattice. The vibrational spectral structure of any pure phase sulfate compound such as $CaSO_4 \cdot 2H_2O$ in the 1100 cm^{-1} region is characteristically broad with little or no resolution of the three component bands. In case of the matrix isolation as occurs in a solid solution, the peak positions shift and a greater degree of resolution can be observed. Solids

identified as containing sulfate by chemical analysis and spectroscopically appeared to be solid solutions were analyzed by X-ray diffraction and differential scanning colorimetry. Both techniques failed to show the presence of a pure phase sulfate compound, specifically indicating that no gypsum was present.

For comparative purposes, the IR spectra of pure calcium sulfite hemihydrate and calcium sulfate dihydrate are shown in Figure 5-1. The absorption structures of interest are the major sulfite band at approximately 980 cm^{-1} and the sulfate band near 1130 cm^{-1}. The structure in the 3200-3600 cm^{-1} and 1600-1700 cm^{-1} ranges are a result of the waters of hydration of the two solids. The absorption bands in the 600-700 cm^{-1} region are due to the sulfite and sulfate ions but are not as distinctive as the major bands.

The infrared spectra of two solid samples from the experimental precipitation studies are shown in Figure 5-2. The upper spectrum is that of the solids precipitated from a solution supersaturated in calcium sulfite hemihydrate and subsaturated with respect to calcium sulfate dihydrate. The band structure encircled is indicative of the IR absorption due to matrix isolated sulfate ion.

The lower spectrum is that of the solids precipitated from a solution supersaturated in both calcium sulfite hemihydrate and calcium sulfate dihydrate. In this case, the structure in the sulfate sorption region shows the presence of sulfate as both pure phase gypsum and in solid solution with calcium sulfite hemihydrate. The presence of gypsum was verified using X-ray diffractions and DSC analyses.

The following is a simplified explanation of the spectral differences of the sulfate ion in a pure phase crystal or in solid

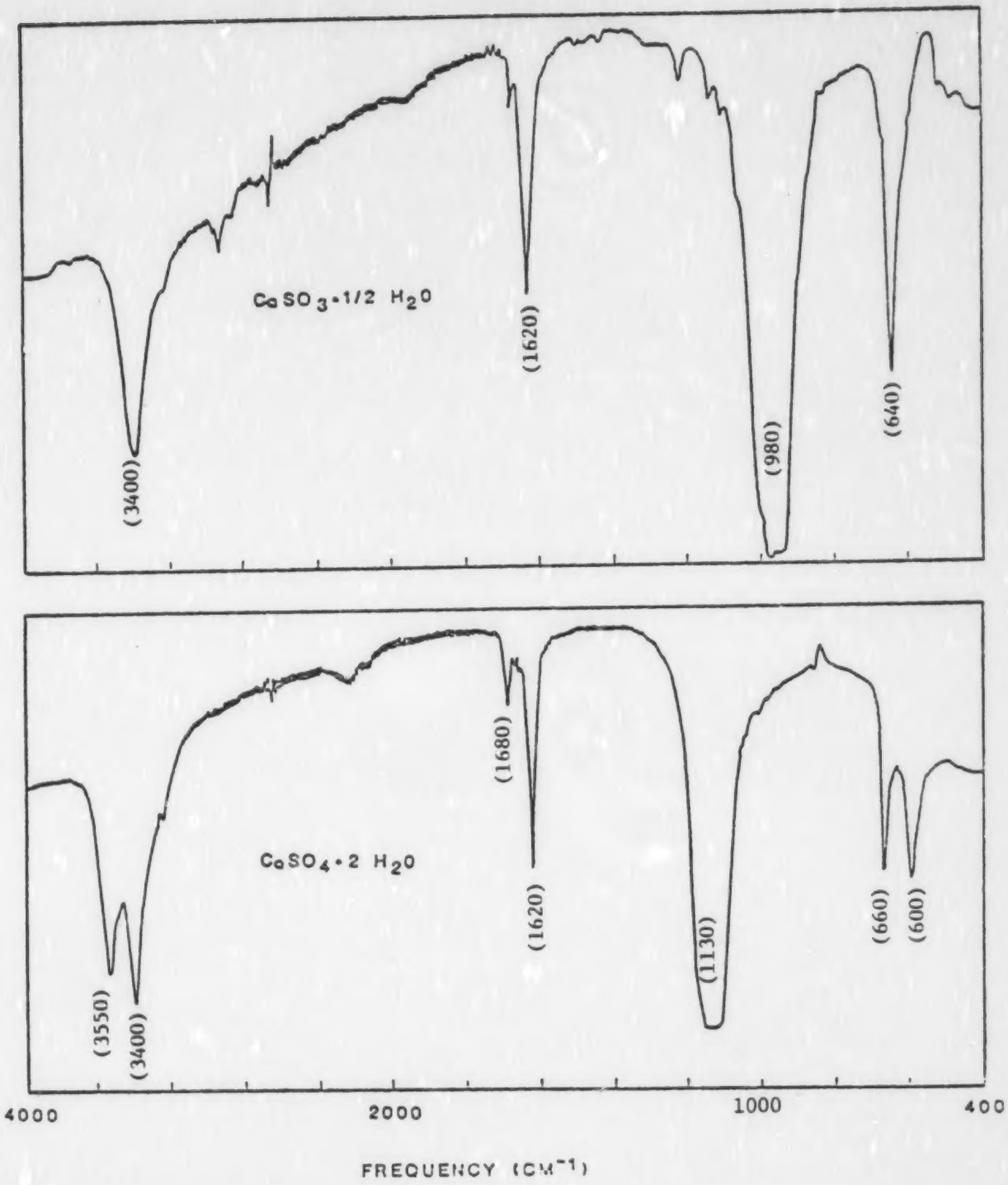


FIGURE 5-1 INFRARED SPECTRA OF PURE CALCIUM SULFITE HEMIHYDRATE AND CALCIUM SULFATE DIHYDRATE

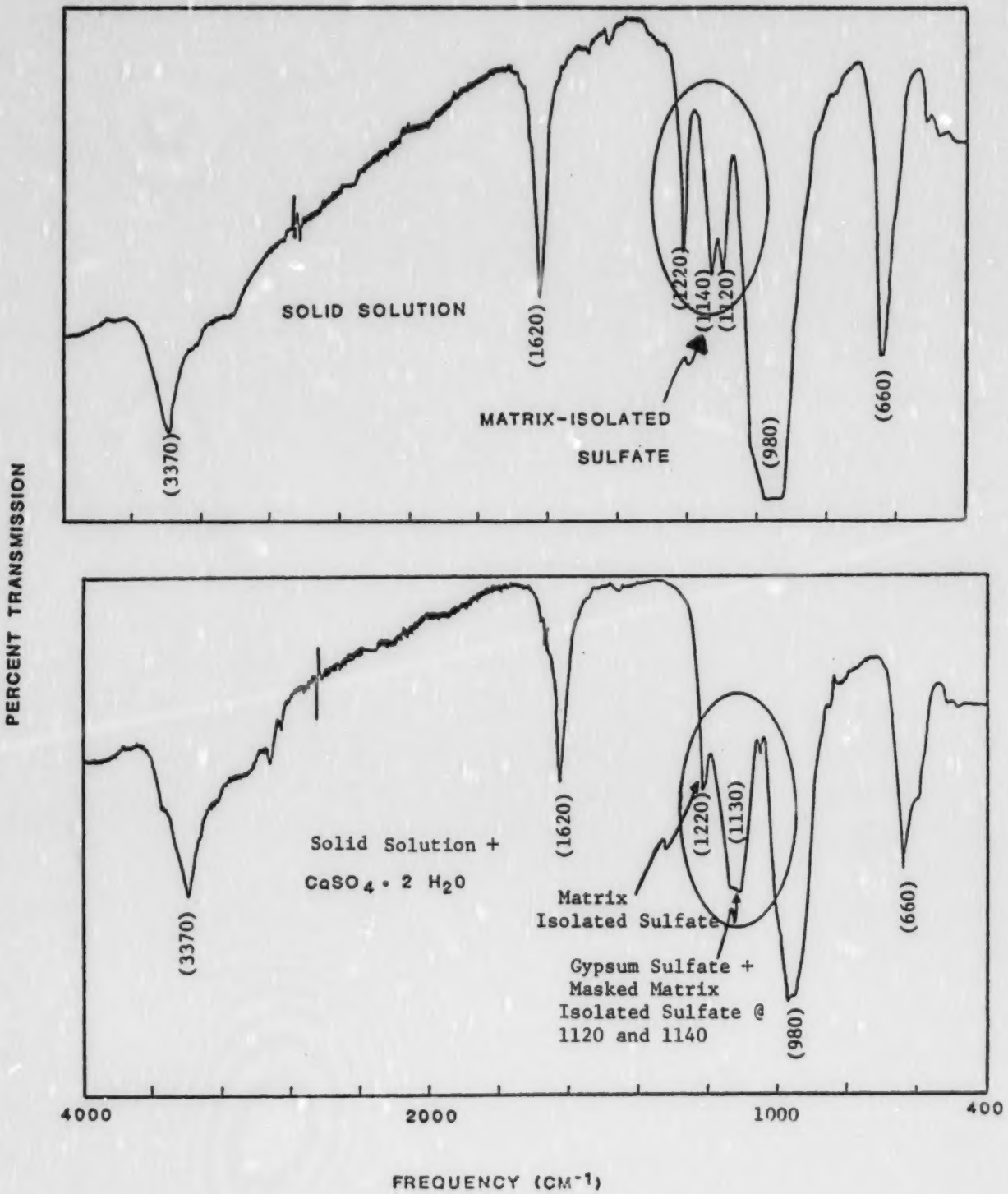


FIGURE 5-2 INFRARED SPECTRA OF REACTOR PRODUCTS

solution with another compound. In the first place, the absorption of electromagnetic radiation in this spectral region results from a coupling of the incident radiation with the vibrational modes of the sulfate ion. Quantum theory predicts three different frequencies. In the case of a pure phase sulfate compound, the frequency range of these vibrations is broadened due to the interaction or coupling of the vibrational modes of neighboring sulfate ions. The matrix isolation of sulfate ions in the solid solution effectively dilutes the sulfate ions as compared to a pure phase system and thus reduces the coupling effect. The frequency shifts and narrowing of the bands are a direct result of the decoupling of the intermolecular interaction of the sulfate ion vibrational modes.

Thus, the combination of these instrumental techniques has been used to verify the existence of the coprecipitation of sulfate with calcium sulfite as a solid solution. In addition, it was demonstrated that the IR spectroscopy can be used to distinguish between the sulfate in a solid solution or as gypsum.

5.1.2 Quantitative Application of Infrared Spectral Analysis

Infrared analysis was also used to quantitatively measure the sulfate concentration in the solid solution. The technique was initially calibrated by comparison of the ratio of the sulfate absorbance at 1220 cm^{-1} to that of the water band at 1620 cm^{-1} with sulfate concentrations determined by the specific chemical method. In the absence of gypsum, the following equation is used to calculate mole fraction of sulfate, $x_{SO_4^{-2}}$ in a solid from the infrared sorption measurements:

$$x_{SO_4^{-2}} = \frac{C_{SO_4^{-2}}}{C_{T_s}} = \frac{C_{SO_4^{-2}}}{2C_{H_2O}} = k\,\frac{A_{SO_4^{-2}}}{A_{H_2O}} = k\,\frac{\left(\log \frac{T_b}{T_m}\right)_{SO_4^{-2}}}{\left(\log \frac{T_b}{T_m}\right)_{H_2O}} \qquad (5\text{-}1)$$

where,

$C_{SO_4^{-2}}$ = the concentration of sulfate in the solids (mole SO_4^{-2}/g sample),

C_{T_s} = the concentration of sulfate plus sulfite in the solids (mole SO_4^{-2} + SO_3^{-2}/g sample),

C_{H_2O} = concentration of the hydration water in the solids (mole H_2O/g sample),

k = a constant,

$A_{SO_4^{-2}}$ = the IR absorbance at 1220 cm^{-1},

A_{H_2O} = the IR absorbance at 1620 cm^{-1}, and

T_b/T_m = the ratio of the percent transmission values at the base line and transmission minimum for the appropriate band.

The correlation of the spectral and chemical results are shown graphically in Figure 5-3. The accuracy limits at the 95% confidence level is ±.02 in the sulfate mole fraction based on a linear least square fit to the data.

5.1.3 Thermal Analysis

Two instrumental techniques based on the thermal properties of solids were evaluated as methods to characterize

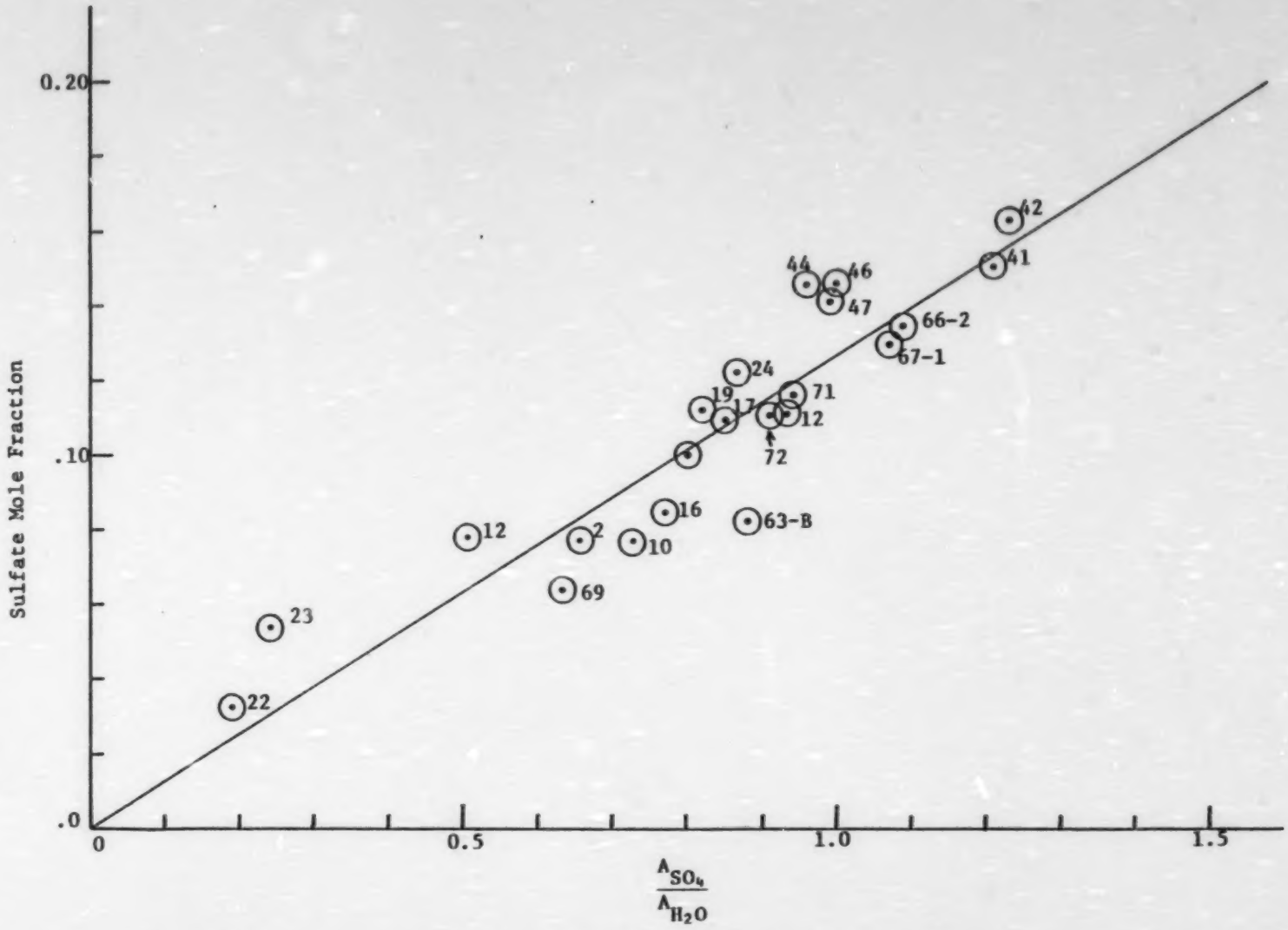


FIGURE 5-3 RESULTS OF INFRARED QUANTITATIVE CORRELATION OF SULFATE MOLE FRACTION WITH THE RATIO OF THE ABSORBANCE OF THE SULFATE BAND (1220 cm^{-1}) WITH THE H_2O BAND (1620 cm^{-1})

the calcium sulfite-sulfate solid solution. The ratio of the waters of hydration to the total sulfur for the solid solutions was investigated by these techniques.

The thermogravimetric analysis (TGA) determines the weight change upon the loss of water as the temperature of the sample is raised past the dehydration temperature. Both the weight loss and the temperature of dehydration are useful to characterize the solids. The other thermal technique is differential scanning colorimetry (DSC). The enthalpy change as a function of sample temperature is measured by this method.

Quantitative TGA measurements were made on the solids precipitated from Experiments K-47 and K-53. From the weight loss associated with the dehydration of the solid solution samples, solids from Run K-47 were found to contain 3.8±.2 mmole H_2O/gram and those from Run K-53 consisted of 3.9±.2 mmole H_2O/gram. These two values give a mole ratio of waters of hydration to total sulfur of .50 and .52 respectively. If the sulfate had been associated with two waters of hydration, a mole ratio of approximately .7 would be expected.

Differential scanning colorimetry was also used to characterize the precipitated solids by monitoring the enthalpy change as a function of temperature. Phase changes, marked by rapid changes in the heat capacity, were observed in the temperature ranges of 120-140°C for gypsum and 350-430°C for calcium sulfite hemihydrate and the solid solutions. These changes are associated with the loss of waters of hydration. A DSC scan of solids from Run K-37 is shown in Figure 5-4. Additional scans of the solids from other runs are included in Appendix E.

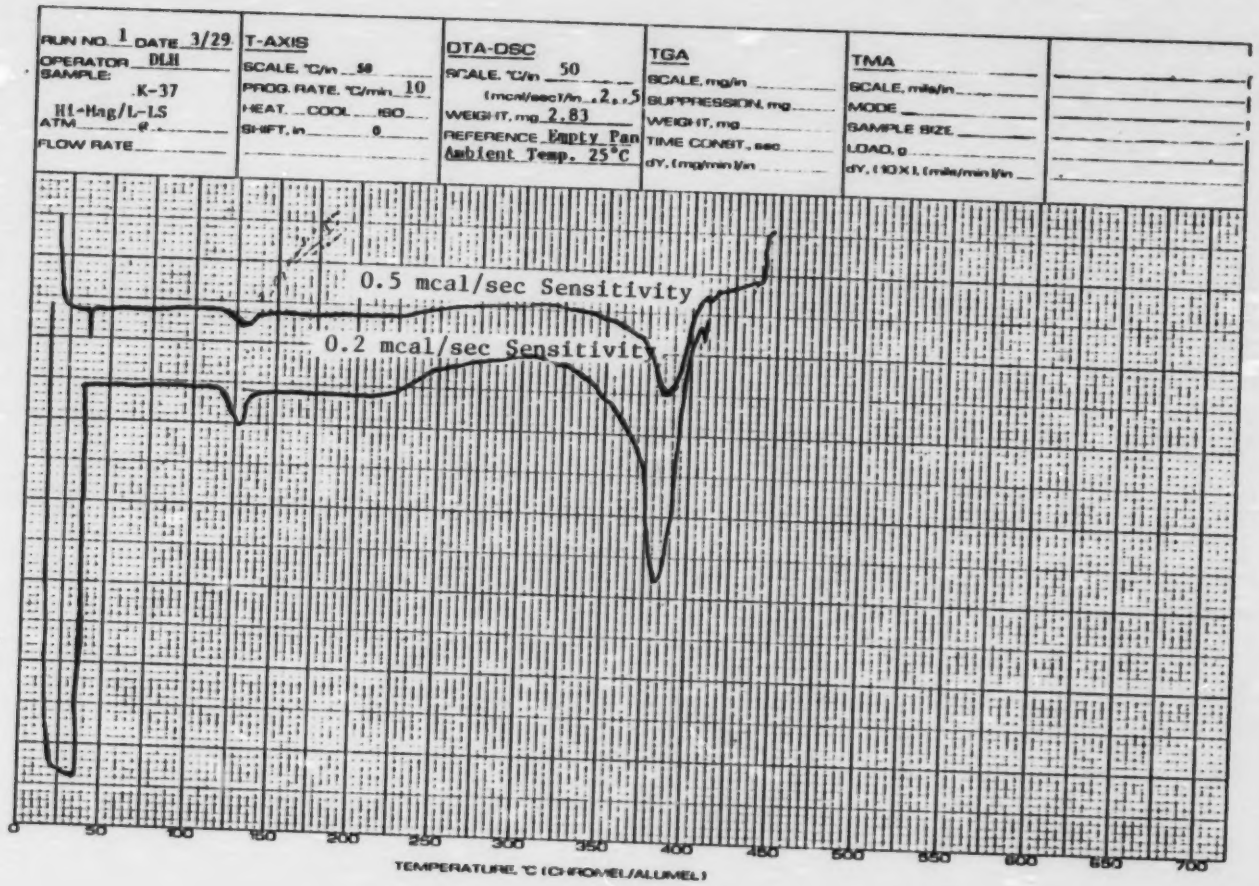


FIGURE 5-4 DIFFERENTIAL SCANNING CALORIMETRY PATTERN OF PRECIPITATED SOLIDS OF KINETIC RUN 37

The change in enthalpy at 120-140°C for the solids from K-37 results from the endothermic dehydration of gypsum. The second change at 350-400°C is the dehydration of the solid solution. Solids in which no gypsum was found also showed no enthalpy change at 120-140°C.

Three distinct patterns have been observed in the 350-430°C range which result from the dehydration of $CaSO_3 \cdot \frac{1}{2}H_2O$ and solid solution. These include an endothermic reaction at 410°C, and a complex endothermic reaction in the range of 350-400°C. Possible explanations for the three different patterns include a different crystal structure of the calcium sulfite hemihydrate resulting from impurities, such as sulfate, in the crystal and/or particle size. X-ray powder diffraction patterns have identified only one crystalline structure of calcium sulfite hemihydrate. This pattern is consistent with literature values (TE-055) and standards prepared in the laboratory. The complex endothermic reactions between 350-400°C were observed only in runs utilizing the grinder in line. This is a strong indication that particle size may have an effect on the temperature of dehydration of the calcium sulfite hemihydrate during analysis by DSC.

6.0 DISCUSSION OF RESULTS

The interpretation of the experimental results presented in Section 5.0 are discussed in this section. The effects of the tested parameters on the sulfate content of the precipitated solids are evaluated and correlations are made where appropriate.

Much of the experimented data reported in Section 5.0 is invalidated by the occurrence of one or more operational difficulties. While these results were reported for completeness, they were not included in the data used to arrive at the conclusions presented in this section. Possible reasons for some of these difficulties are discussed.

A series of long term equilibration studies were conducted to determine the stability of the solid solutions in the presence of solutions of similar concentrations as the liquors from which they were initially precipitated. In addition, pure calcium sulfite hemihydrate crystals were also subjected to long term contact with these liquors to determine the degree of sulfate incorporation near the equilibrium of calcium sulfite hemihydrate. Solid solution solids were placed in water saturated with calcium sulfite but with no sulfate present.

The solids and test solutions were sealed into cylindrical plexiglas vessels with several ceramic grinding cylinders. The containers were maintained in an inert atmosphere at 50°C for the duration of the tests. The samples were mechanically rotated to provide grinding of the solids to expose fresh surfaces throughout the test period.

The solid solution in contact with the liquor containing no sulfate showed a small decrease, $\sim$0.01 mole fraction, in sulfate content. The sulfite in contact with liquor almost saturated with

gypsum gained a small amount of sulfate (~0.01 mole fraction). Solid solutions in contact with their equilibrium liquors showed no change. Solids containing gypsum had the gypsum dissolved when in contact with the subsaturated liquors.

This indicates that:

- once formed the interior of a solid solution particle is protected from the solution by low solid state diffusion and

- gypsum cannot co-exist with solid solution in a subsaturated solution.

The specific classifications of experimental difficulties experienced were:

- supersaturation of the reactor liquor with respect to gypsum,

- the presence of gypsum in the precipitated solids as identified by infrared spectroscopy, x-ray diffraction or differential scanning colorimetry,

- calcium carbonate in the solids in excess of 60 weight percent, and

- insufficient approach to system lineout with respect to the precipitated solids, i.e., $e^{-T/\tau} > .35$.

The experiments disregarded on the basis of these criteria are listed in Table 6-1. The remainder of the experimental runs which were used to develop the correlations presented in this section are given in Table 6-2.

TABLE 6-1. EXPERIMENTAL RESULTS INVALIDATED

	Liquid Analyses (moles/ℓ)						Relative Saturation				
Run #	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction Sulfate in Solids	Classification	Deletion Criteria
E-5	16.3	-	3.1	1.8	.58	15.6	1.76	.41	.17	Clear Liquor	Gypsum
E-3	9.1	-	19.4	39.6	.64	8.4	2.30	.15	.07	Clear Liquor	$e^{-T/\tau} = .45$
E-15	1.13	-	5.5	4.10	1.25	.13	2.54	<.01	.01	Clear Liquor	$e^{-T/\tau} = .38$
E-22	12.8	87.2	4.0	62.4	3.02	55.8	3.77	.22	.16	Clear Liquor (Mg)	$e^{-T/\tau} = .71$
E-23	12.8	91.5	4.0	60.2	2.76	56.1	3.35	.22	.12	Clear Liquor (Mg)	$e^{-T/\tau} = .48$
E-26	8.83	-	24.4	26.0	3.56	4.55	4.52	.08	.23	Lime	Gypsum
E-27	21.0	-	83.0	87.6	4.60	34.0	8.52	.48	.85	Lime	r.s. = 1.06
E-28	28.0	-	146	96.4	2.17	25.5	8.23	.55	.49	Lime	r.s. = 1.30
E-29	16.4	-	173	93.0	2.41	59.4	5.55	.45	.69	Lime	r.s. = 1.00
E-33	33.0	-	56.2	88.4	8.3	26.1	13.1	.63	.26	Limestone	Gypsum and r.s. = 1.39
E-34	32.0	-	46.8	75.4	7.0	24.8	12.9	.59	.19	Limestone	r.s. = 1.34
E-35	17.6	-	94.8	76.0	6.6	39.2	7.80	.44	.21	Limestone	Gypsum
E-37	12.1	408	2000	656	81.5	427	14.0	.34	.19	Limestone (Mg)	Gypsum
E-40	29.2	612	103	579	23.4	325	9.8	.72	.44	Lime (Mg)	r.s. = 1.60
E-41	25.9	517	280	639	54.6	232	1.9	.47	.15	Lime (Mg)	r.s. = 1.08
E-44	25.7	560	60.7	766	17.1	200	7.4	.46	.14	Lime (Mg)	r.s. = 1.01
E-45	27.7	529	48.0	817	14.9	207	6.7	.52	.80	Lime (Mg)	r.s. = 1.15
E-59	7.26	-	38.8	-	9.26	14.4	8.0	.16	.18	Limestone	$e^{-T/\tau} = .58$

(continued)

TABLE 6-1 (continued)

Run #	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction Sulfate in Solids	Classification	Deletion Criteria
E-63	14.9	-	110	-	19.4	61.2	6.10 ..	.46	.24	Limestone	$e^{-T/\tau} = .17$
E-63B	12.6	782	548	-	97	1010	5.07	.68	.09	Limestone (Mg)	r.s. = 1.17
E-64	13.8	-	1420	784	38.7	290	10.1	.40	.09	Limestone	$CaCO_3 > .6$
E-65	7.75	574	310	-	155	700	5.8	.31	.05	Limestone (Mg)	$CaCO_3 > .6$
E-66	7.0	516	312	-	148	647	5.7	.29	.05	Limestone (Mg)	$CaCO_3 > .6$
E-67	6.98	436	332	-	159	527	7.5	.19	.03	Limestone (Mg)	$CaCO_3 > .6$
E-68	7.79	404	296	-	92	448	4.1	.27	.04	Limestone (Mg)	$CaCO_3 > .6$

r.s. = relative saturation of $CaSO_4 \cdot 2H_2O$

TABLE 6-2. EXPERIMENTAL RESULTS FOR CORRELATIONS

	Liquid Analyses (moles/l)						Relative Saturation			
Run #	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction Sulfate in Solids	Classification
E-8	6.2	-	0.1	.1	.56	5.6	1.93	.11	.09	Clear Liquor
E-9	8.3	-	1.4	.1	.46	7.8	1.70	.18	.13	Clear Liquor
E-10	1.1	-	-	-	.77	0.3	1.90	<.01	.01	Clear Liquor
E-11	9.4	-	-	-	.39	8.7	1.44	.21	.12	Clear Liquor
K-2	8.5	-	16.4	18.7	.72	8.2	2.54	.14	.10	Clear Liquor
K-6	8.9	-	17.4	17.6	.64	7.6	2.28	.14	.06	Clear Liquor
K-8	12.7	-	27.6	25.6	.61	12.3	2.29	.23	.13	Clear Liquor
K-9	11.7	-	36.8	37.2	.67	11.0	2.35	.20	.14	Clear Liquor
K-10	9.7	-	51.6	56.8	.77	10.1	2.63	.14	.08	Clear Liquor
K-11	12.6	-	24.8	27.4	.70	11.3	2.58	.22	.14	Clear Liquor
K-12	12.0	-	25.2	25.0	.66	11.9	2.45	.23	.13	Clear Liquor
K-13	11.3	-	24.4	27.4	.72	11.7	2.59	.21	.10	Clear Liquor
K-14	1.15	-	5.9	4.20	1.07	.21	2.29	<.01	.01	Clear Liquor
K-16	13.8	-	38.2	30.8	.87	14.3	3.22	.25	.10	Clear Liquor
K-17	15.9	-	29.6	33.6	.72	14.4	2.72	.29	.11	Clear Liquor
K-18	19.9	-	20.4	42.0	.67	11.9	2.65	.29	.13	Clear Liquor
K-19	17.3	-	34.0	39.2	.78	16.0	2.93	.32	.12	Clear Liquor
K-20	17.1	-	32.6	40.9	.71	17.3	2.66	.35	.11	Clear Liquor
K-21	17.4	-	31.8	42	.70	15.6	2.66	.33	.12	Clear Liquor

(continued)

TABLE 6-2 (continued)

	Liquid Analyses (moles/l)						Relative Saturation			
Run #	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction Sulfate in Solids	Classification
K-29	11.4	-	35.8	33.0	1.49	11.1	5.33	.19	.15	Lime
K-30	12.3	-	114	14.0	13.3	37.4	5.50	.10	.13	Limestone
K-31	13.1	-	184	26.5	10.1	61.5	5.96	.18	.13	Limestone
K-32	12.6	-	78	83.9	8.6	26.9	8.41	.39	.20	Limestone
K-38	11.1	-	60	32.6	5.12	21.6	7.54	.19	.16	Lime
K-39	19.4	549	228	594	50.2	322	9.9	.36	.16	Lime (Mg)
K-42	28.3	481	135	518	35.7	257	13.3	.32	.16	Lime (Mg)
K-46	26.6	248	40.0	384	10.3	118	6.7	.43	.15	Lime (Mg)
K-47	22.7	354	45.4	634	12.9	103	6.2	.26	.15	Lime (Mg)
K-48	30.8	520	40.0	880	10.3	85.4	5.4	.25	.16	Lime (Mg)
K-49	25.9	500	44.4	853	7.69	93	3.19	.39	.15	Lime (Mg)
K-50	9.53	-	40.4	43.3	1.90	7.8	6.6	.03	.09	Clear Liquor
K-51	9.02	-	41.0	41.0	1.84	8.66	6.4	.10	.09	Clear Liquor
K-52	9.01	-	42.8	40.6	1.59	7.90	5.4	.11	.11	Clear Liquor
K-53	6.92	-	43.6	39.6	1.44	9.66	4.3	.13	.11	Clear Liquor
K-56	14.7	-	42.0	44.2	2.08	8.76	7.9	.14	.09	Clear Liquor
K-60	4.24	-	45.6	-	18.9	14.4	3.1	.085	.12	Limestone
K-61	4.20	-	70.4	-	20.5	23.7	2.16	.125	.08	Limestone

(continued)

TABLE 6-2 (continued)

	Liquid Analyses (moles/ℓ)						Relative Saturation			
Run #	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$SO_3^{=}$	$SO_4^{=}$	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction Sulfate in Solids	Classification
K-62	10.78	-	128	-	12.8	52.8	7.46	.24	.17	Limestone
K-69	9.3	-	26.0	18.4	.70	2.06	2.4	.04	.06	Clear Liquor
K-70	8.59	-	44.6	18.2	.73	9.67	2.3	.14	.11	Clear Liquor
K-71	10.1	-	43.6	42	2.24	9.06	5.3	.14	.12	Clear Liquor

r.s. = relative saturation of $CaSO_4 \cdot 2H_2O$

6.1 Effect of Relative Saturation of $CaSO_4 \cdot \frac{1}{2}H_2O$

The aqueous phase relative saturation of calcium sulfate hemihydrate was found to exhibit the most significant effect on the composition of the solid solution based on the results of the laboratory studies conducted by Radian. These measurements showed that the sulfate content of the solid solution varies most rapidly with the calcium sulfate hemihydrate concentration between relative saturation values of 0-0.2. At values higher than 0.2, the change in solid composition is less rapid. At compositions above a relative saturation of 0.45, the solution becomes supersaturated in gypsum. Further precipitation of sulfate may occur as gypsum as well as in the solid solution. The presence of gypsum in the solids complicates the determination of the sulfate content of the solid solution.

The relation between the sulfate mole fraction in the solids and the relative saturation of $CaSO_4 \cdot \frac{1}{2}H_2O$ in the aqueous phase is shown graphically in Figure 6-1. This correlation represents only the experiments referred to as clear liquor runs in Table 6-2.

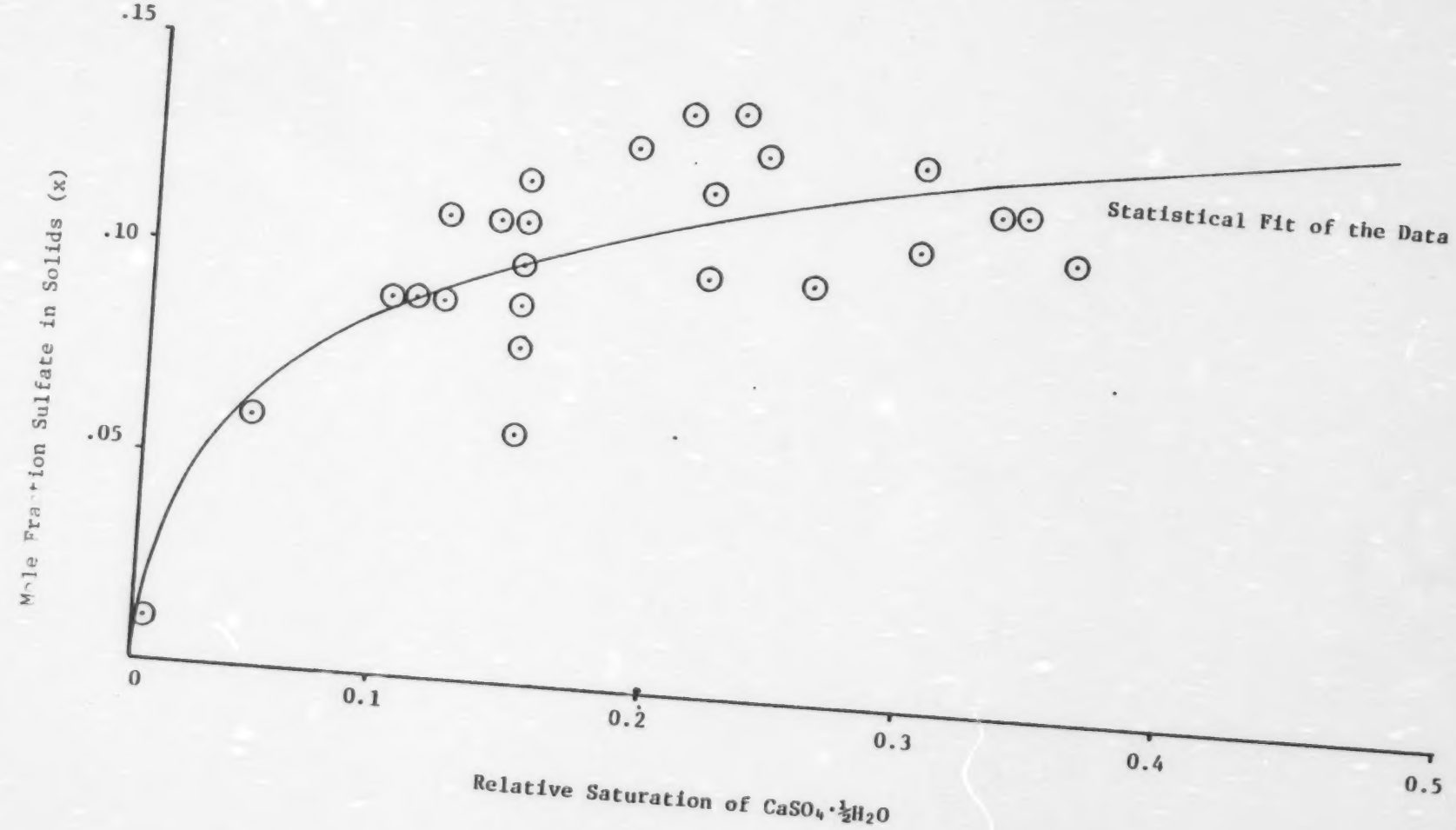
A theoretical fit of the data was made based on the equilibrium relationship derived by P. S. Lowell as developed in Section 3.0. At equilibrium, the relation between the liquid and solids compositions with respect to sulfate can be written as:

$$R.S._{CaSO_4 \cdot \frac{1}{2}H_2O} = \frac{a_{Ca^{++}} \quad a_{SO_4^=} \quad a^{\frac{1}{2}}_{H_2O}}{K_{sp\ CaSO_4 \cdot \frac{1}{2}H_2O}} = \sigma_{CaSO_4 \cdot \frac{1}{2}H_2O} \quad x_{CaSO_4 \cdot \frac{1}{2}H_2O} \qquad (6\text{-}1)$$

The form of the solid phase activity coefficient, σ, was empirically chosen as:

$$\ln \sigma_2 = \alpha_1 + \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O} \qquad (6\text{-}2a)$$

Figure 6-1 Sulfate Content of Solid Solution as a Function of $CaSO_4 \cdot \frac{1}{2}H_2O$ Relative Saturation in Solution, Clear Liquor Studies



or

$$\sigma_2 = \exp(\alpha_1 + \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O}) \qquad (6\text{-}2b)$$

The arbitrary constants, α_1 and α_2, must be determined from experimental data. The mole fraction of sulfate in the solids may be written implicitly as a function of the relative saturation of $CaSO_4 \cdot \frac{1}{2}H_2O$.

$$x_{CaSO_4 \cdot \frac{1}{2}H_2O} = \exp\left(-\alpha_1 - \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O}\right) R.S._{CaSO_4 \cdot \frac{1}{2}H_2O} \qquad (6\text{-}3)$$

or

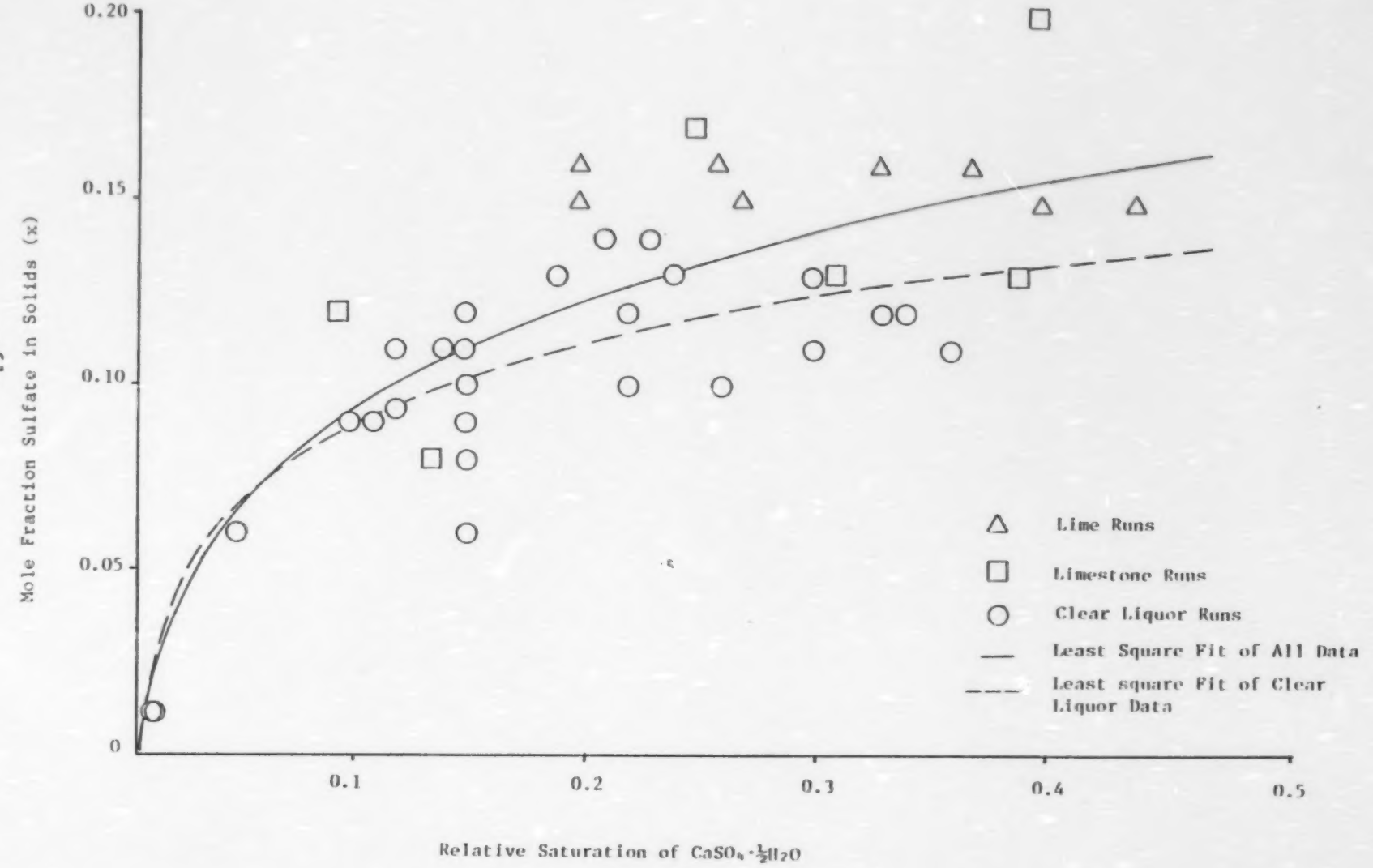
$$R.S._{CaSO_4 \cdot \frac{1}{2}H_2O} = x_{CaSO_4 \cdot \frac{1}{2}H_2O} \exp\left(\alpha_1 + \alpha_2 x_{CaSO_4 \cdot \frac{1}{2}H_2O}\right) \qquad (6\text{-}4)$$

Based upon the data in Figure 6-1, a least squares fit gave values of α_1 and a_2 of -1.94 and 22.5, respectively. Given the sulfate mole fraction, the relative saturation may be calculated directly from Equation 6-4. Given the relative saturation, the sulfate mole fraction may be calculated by an iterative procedure.

The relationship between the mole fraction of solid solution sulfate and the relative saturation of calcium sulfate hemihydrate for all of the acceptable experimental tests, see Table 6-2, is shown in Figure 6-2. A least squares fit gave values of α_1 and α_2 of -1.45 and 15.9, respectively. The theoretical fit to the clear liquor data is included for comparison in Figure 6-2.

Although a slight increase is noted in the predicted sulfate content in the solids from a fit to all of the data as compared to the clear liquor data, the difference is small compared to the overall scatter in the data.

Figure 6-2 Comparison of Lime and Limestone Experiments With The Clear Liquor Runs



The precipitation rate of the solid solution appears to be a function of the sulfite relative saturation. The sulfate precipitation rate would be equal to the solid solution precipitation rate times the mole fraction sulfate as calculated from Equation 6-3.

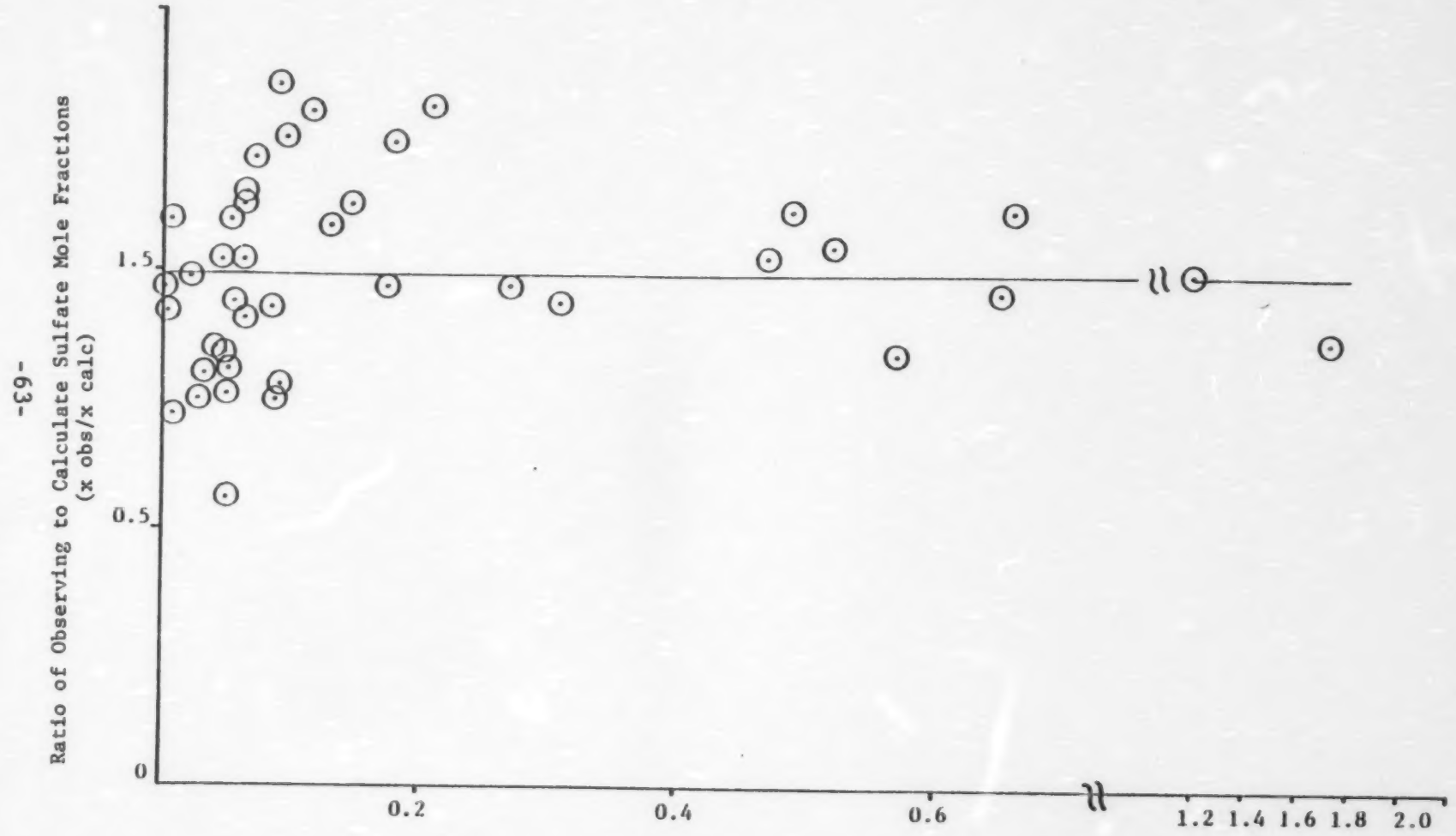
6.2 Effect of Calcium Sulfite Precipitation Rate

The possibility exists that the inclusion of sulfate in the calcium sulfite hemihydrate lattice is a kinetic phenomenon. If this is the case, one would expect a dependence of sulfate in the solid as a function of precipitation rate.

Radian laboratory experimental results do not show any discernible dependence of sulfate content on the precipitation rate. This lack of dependence of sulfate in the solids as a function of precipitation rate is shown graphically in Figure 6-3.

The data in Figure 6-3 span a range of precipitation rates from 0.001-1.73 mmoles/g-min. The sulfate content of the solids in this correlation was corrected for the effect of calcium sulfate hemihydrate relative saturation by dividing the measured sulfate mole fraction by the mole fraction predicted by Equation 6-4. A linear least square fit was made of the data which showed the results to be uniformly scattered about a mole fraction ratio of one. This indicates that even though there is considerable scatter in the data no consistent dependence on the precipitation rate is evident.

Figure 6-3 Sulfate Content of Solids as a Function of $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate



6.3 Comparison of Lime and Limestone Tests With Clear Liquor Results

Experimental studies were conducted to measure the influence of lime and limestone on the formation of the calcium sulfite-sulfate solid solution. Any effects of lime and limestone were expected to result from increased precipitation effects resulting from localized areas of high calcium sulfite hemihydrate relative saturations. Such concentration gradients may arise from the dissolution of lime or limestone solids. The experimental data are compared graphically to the clear liquor results in Figure 6-2. The mole fraction of sulfate in the solids precipitated from the lime experiments are higher than in the clear liquor solids. However, due to the limited number of data points and the coincidence of high levels of magnesium and chloride concentrations in the test solutions with most lime runs, the evidence is inconclusive that the presence of lime substantially enhance the sulfate content of the solid solution.

The limestone data scatter around the clear liquor line and appear to have an enhanced sulfate mole fraction. The relatively small number of data points again makes drawing conclusions risky. Again coincidence of high magnesium and chloride concentration clouds the issue.

6.4 Effects of High Levels of Chloride and Magnesium

The effects of magnesium and chloride on the sulfate content of the solids is difficult to ascertain from the experimental data. The primary problem arises from the fact that the only successful reactor test at high magnesium and chloride levels were also lime runs. These results are displayed graphically in Figure 6-4. Further characterization of the

precipitation from solutions high in magnesium and chloride are needed to quantify the effects of these ions.

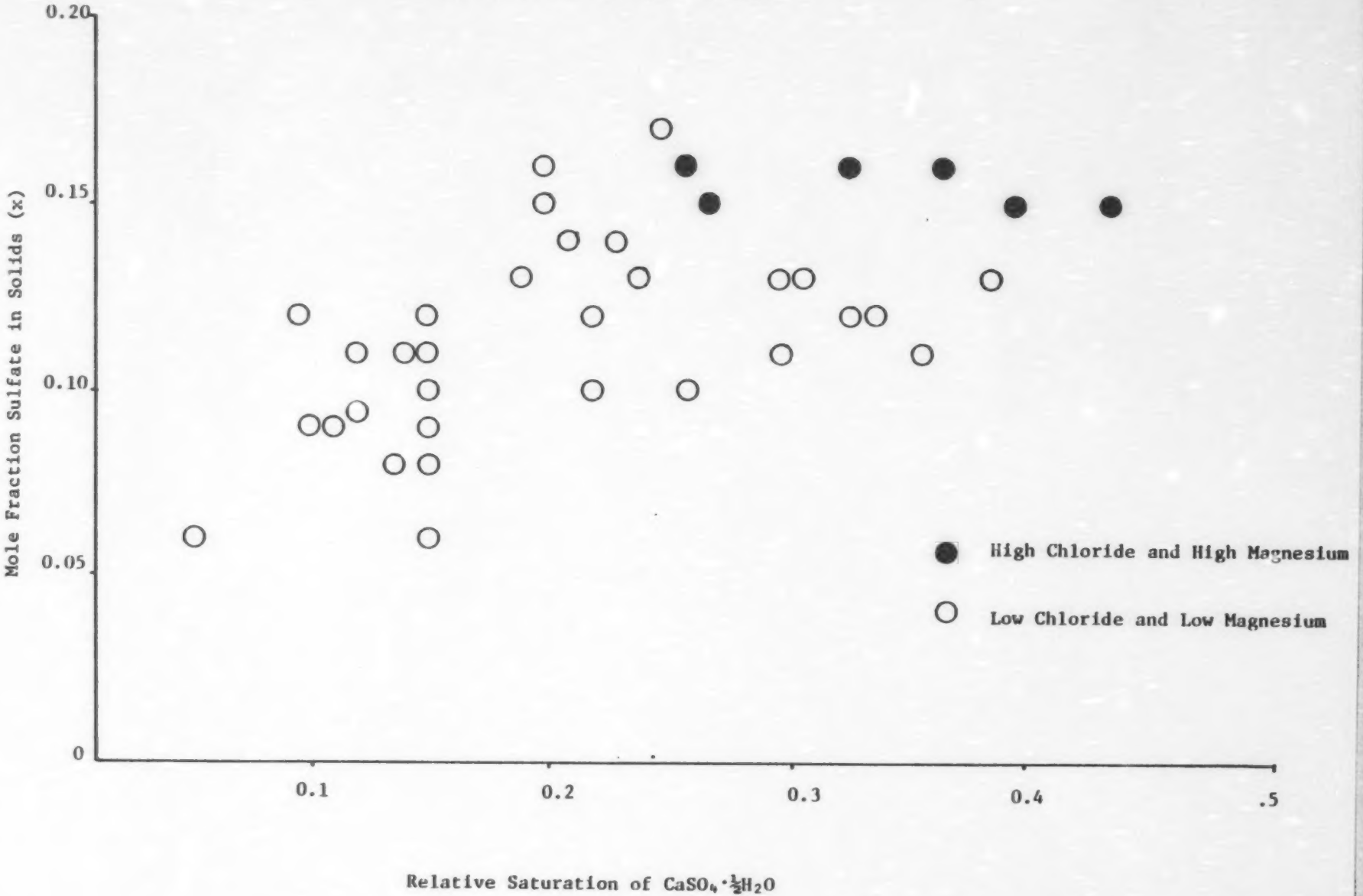
The precipitation rate of calcium sulfite appeared to be inhibited by the high concentrations of these ions. A similar effect was also found when low concentrations of carbonate were present in the liquor.

6.5 Effect of Temperature

Experimental measurements carried out at 40, 50, and 60°C showed only a slight effect of temperature on the coprecipitation of calcium sulfate and sulfite. This conclusion is based on results from five experimental runs, K-50, 51, 52, 53, and 56, with similar solution composition and calcium sulfite precipitation rates.

In order to normalize the results the ratio of observed to calculated values of sulfate mole fraction in the solid was computed. This ratio is presented in Figure 6-4 as a function of temperature. The temperature effect in Figure 6-4 represents a deviation of 0.8% per degree C from 50°C which is the temperature at which most of the data were taken.

Figure 6-4 Effect of High Chloride and Magnesium Concentrations Of Sulfate Content of Solid Solution



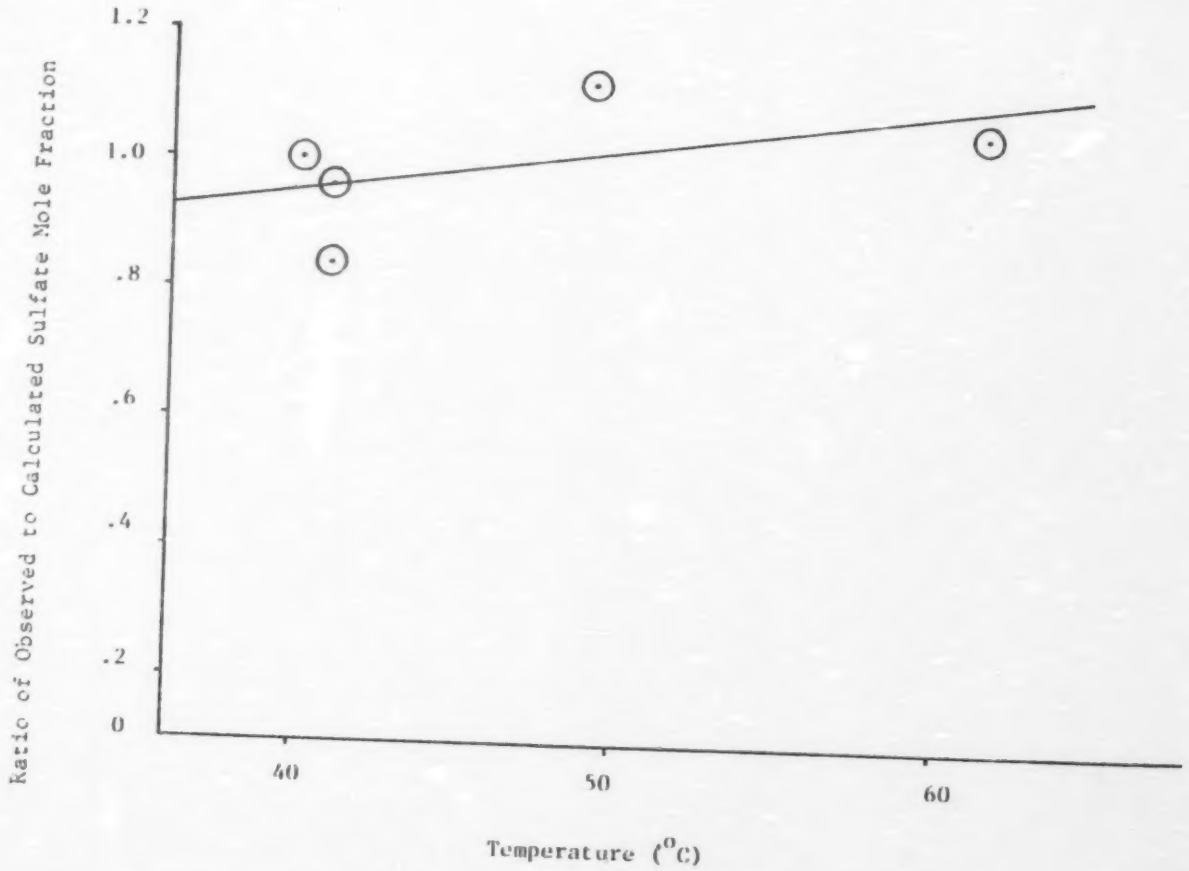


Figure 6-5 The Effect of Temperature on Sulfate Concentration in the Solids

7.0 REVIEW OF PLANT AND PILOT PLANT DATA

As part of this program pilot plant and full-scale system performance data relating to the coprecipitation phenomenon which were available to EPA were reviewed by Radian. The purpose of this data review was twofold:

- to define ranges of operation conditions under which coprecipitation is observed to occur. This information is important because it identified the variables to be considered in the experimental phases of the program, and

- to provide a basis for comparing the results obtained in the Radian laboratory experiments with actual scrubber performance.

The Environmental Protection Agency has obtained a considerable amount of data on calcium sulfite/sulfate coprecipitation in lime and limestone wet scrubbing systems in pilot plant studies conducted at Research Triangle Park, North Carolina. In addition, data have been supplied to EPA by Imperial Chemical Industries (ICI) on their Bankside Power Plant, by Arthur D. Little, Inc. (ADL) in the report "Scale Control in Limestone Wet Scrubbing Systems", by Bechtel Corporation on the Shawnee Test Facility, and by Louisville Gas and Electric (LG&E) on their Paddy's Run Scrubber.

The ICI and ADL data transmitted to us were incomplete as far as this program was concerned since no liquor compositions or hold tank data were reported. Complete liquid and solid phase analyses for a significant fraction of the LG&E test runs were

also not available. For this reason, almost all of the test data considered are based upon EPA/RTP pilot plants and Bechtel-Shawnee studies.

Review of EPA/RTP data included conversion of reported liquid and solid concentrations from a weight basis to a molar basis. These concentrations were then input to Radian's aqueous ionic equilibrium program for calculation of solution activities and relative saturations. Sulfite and sulfate mole fractions were calculated from solids concentrations. Calcium sulfite precipitation rates in the sealed hold tanks were calculated from reported inlet and outlet liquor compositions and flow rates. Calcium sulfate precipitation rates were calculated from the system oxidation rate and sulfite precipitation rate. EPA/RTP and LG&E data are presented in Appendix B along with calculated activities, relative saturations and mole fractions. These values were used in defining the variables considered in the experimental phase of this project.

The EPA/RTP, LG&E and Shawnee data were analyzed according to the theoretical framework developed by Radian and in view of the laboratory results of this experimental program. The theoretical framework and Radian experimental data suggest that the sulfate mole fraction is best correlated with the relative saturation of calcium sulfate hemihydrate. The results of a graphical analysis of this correlation for the EPA/RTP and LG&E data is shown in Figure 7-1.

There is a significant degree of scatter in the data. Part of this scatter is very likely due to analytical inaccuracies in the determination of the sulfate content of the solids. Correlation of these pilot unit data with liquid phase properties is difficult since a change in one parameter is usually accompanied by other changes. The high degree of scatter observed in

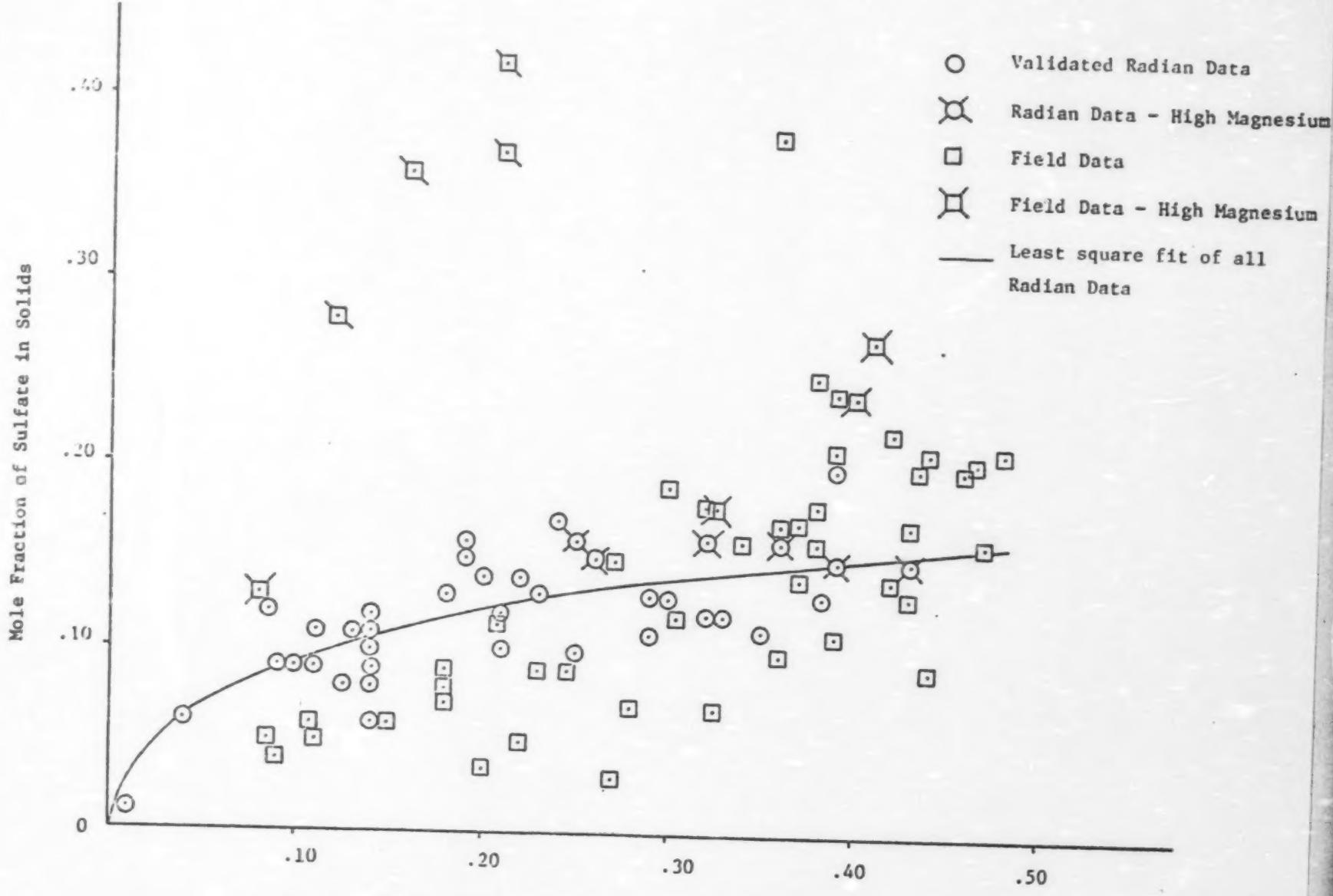


FIGURE 7-1 CONCENTRATION OF SULFATE IN THE SOLIDS AS A FUNCTION OF THE $CaSO_4 \cdot \frac{1}{2}H_2O$ RELATIVE SATURATION IN THE AQUEOUS PHASE

the field limestone runs made at high liquid phase magnesium concentrations cannot be solely explained by analytical inaccuracies. This scatter can be explained by the experimental difficulties associated with the sampling and sample handling of slurries containing high liquid phase magnesium sulfate concentrations.

The EPA/RTP pilot plant data show that gypsum unsaturated operation is possible and that the relative saturation of calcium sulfate does affect the sulfate content in the solids even in unsaturated operation.

Experimental data from EPA's alkali scrubbing test facility located at TVA's Shawnee Power Station in Paducah, Kentucky, were also examined. These data covered testing between June 1975 and January 1976 and were furnished to Radian by Bechtel Corporation. The report included experimental data from lime and limestone runs.

Liquid and solid phase analytical data for this period of Shawnee operation have been examined. The sulfate content of the solids has been compared with the liquid phase relative saturation of calcium sulfate as a function of time for both limestone and lime runs. This allows the solids residence time to be included in the analysis as the residence time of the solids is in the order of days. Graphical results of these comparisons are presented in Appendix B. An example is shown in Figure 7-2. In general, an increase in the calcium sulfate relative saturation was accompanied by an increase in the sulfate mole fraction of the solids. Also, a decrease in gypsum relative saturation to subsaturated operation was accompanied by a general decrease in the sulfate concentration in the solids.

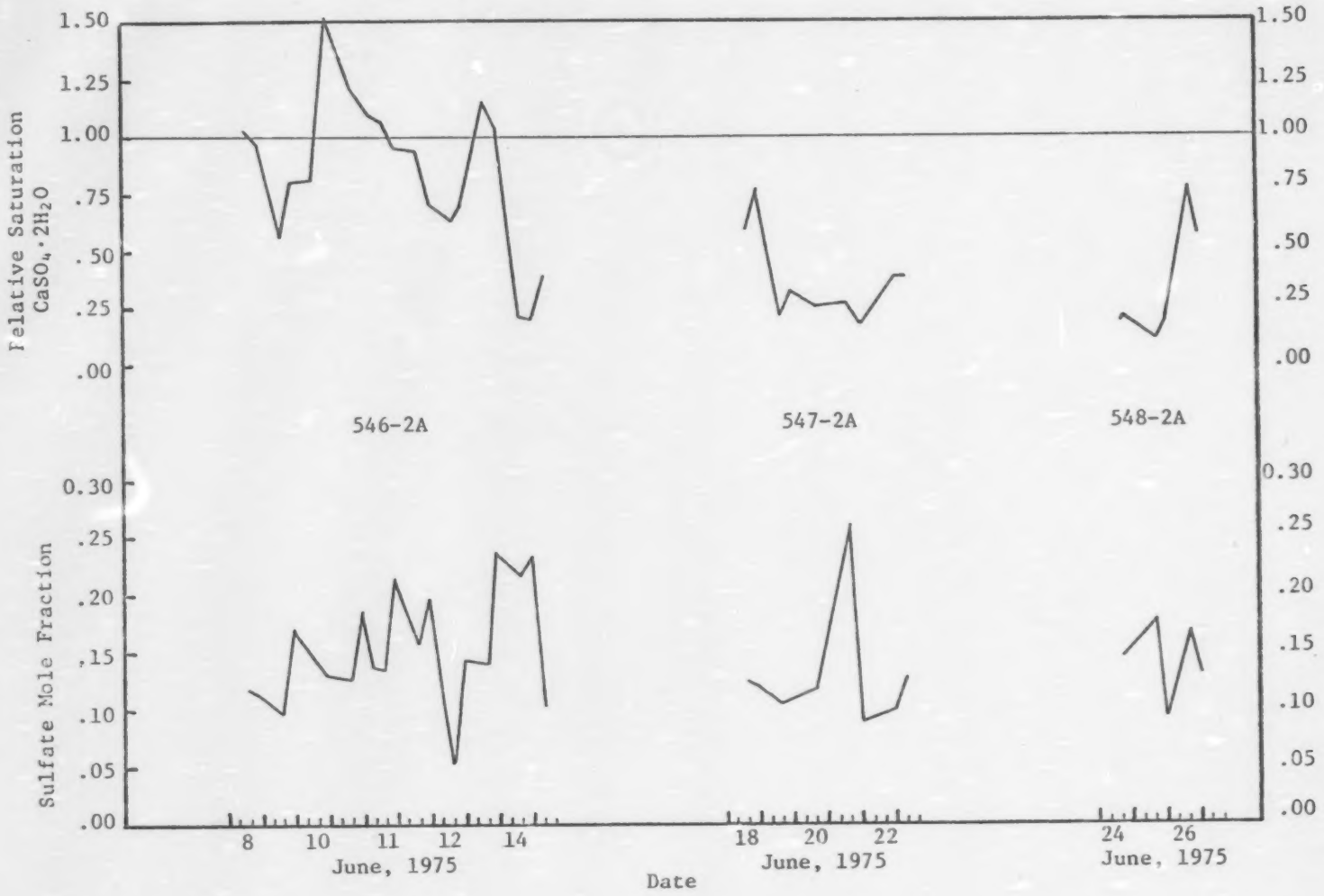


FIGURE 7-2 EXAMPLE OF RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

8.0 RECOMMENDATIONS

Many of the factors influencing the sulfate content of the solid solution have been characterized during this program. However, more precipitation measurements are required to fully quantify the effects of high concentrations of magnesium and chloride.

Additional studies are also recommended to better describe the role that the dissolution of lime or limestone may have on the amount of sulfate coprecipitated with calcium sulfite hemihydrate. Modification of the flow-through reactor used in the program just completed would be required in order to attain greater limestone utilization. The large excesses of limestone with the product crystals interfered with the chemical characterization of the solid solution solids precipitated in this program.

Even though some refinement may still be required to allow exact prediction of the sulfate content of the solid solution, the results produced thus far provide a basic understanding of those factors that most significantly influence the composition of the coprecipitate.

Development of a relationship to predict the sulfate content of the solid solution which includes the effects of such species as chloride and magnesium and the dissolution of lime or limestone may explain more of the field scrubber results. However, many of the apparent inconsistencies between laboratory results and field data may, in fact, be due to sampling and analytical difficulties arising under field conditions.

During the experimental phase of this program two related phenomena were encountered. First, the presence of

high concentration of magnesium and chloride in the solution appear to have an overall inhibiting effect on the precipitation rate of calcium sulfite and/or the solid solution. The presence of small quantities of dissolved carbonate also exhibited an inhibitive effect on the precipitation rate. Since this rate is very important in the overall design and operation of lime and limestone scrubbers operating at low oxidation, an understanding of the exact effect of these species on the precipitate rate is needed.

The second finding relates to the apparent coprecipitation of carbonate with calcium sulfite. Some preliminary assessments of infrared spectra of some of the limestone products indicate the presence of carbonate in the calcium sulfite hemihydrate crystal. This could have a significant effect on the maximum utilization of limestone achievable at low oxidation conditions.

Since the subsaturated operation of an SO_2 scrubbing system based on the addition of lime or limestone will depend on the degree of oxidation of sulfite to sulfate, an understanding of the parameters important in this oxidation process is important. A full characterization of the sulfite oxidation mechanism may lead to a method of controlling the oxidation rate. For example, some Russian studies, in which sulfite oxidation rates were measured as a function of pH and transition metal concentrations, have shown that under certain conditions the presence of some of these metals can actually inhibit the oxidation. It is recommended that a controlled laboratory study be conducted to more fully investigate these preliminary findings and relate this information to the control of oxidation in an actual scrubbing system.